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JOURNAL
OF THE
INDIAN CHEMICAL SOCIETY

VOL. XXXIII JUNE, 1956 No. 6

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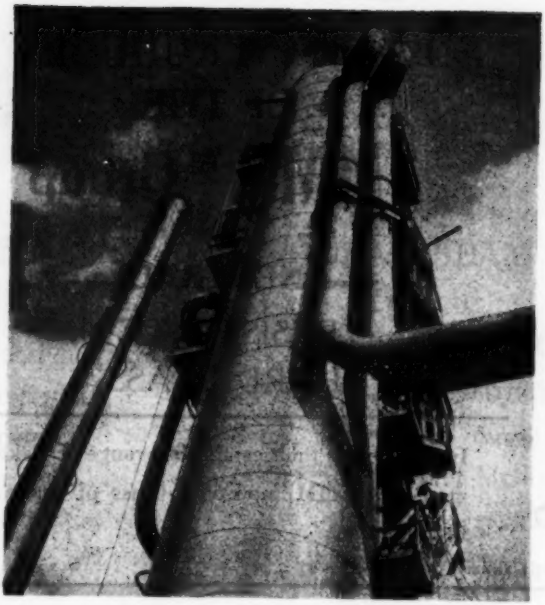

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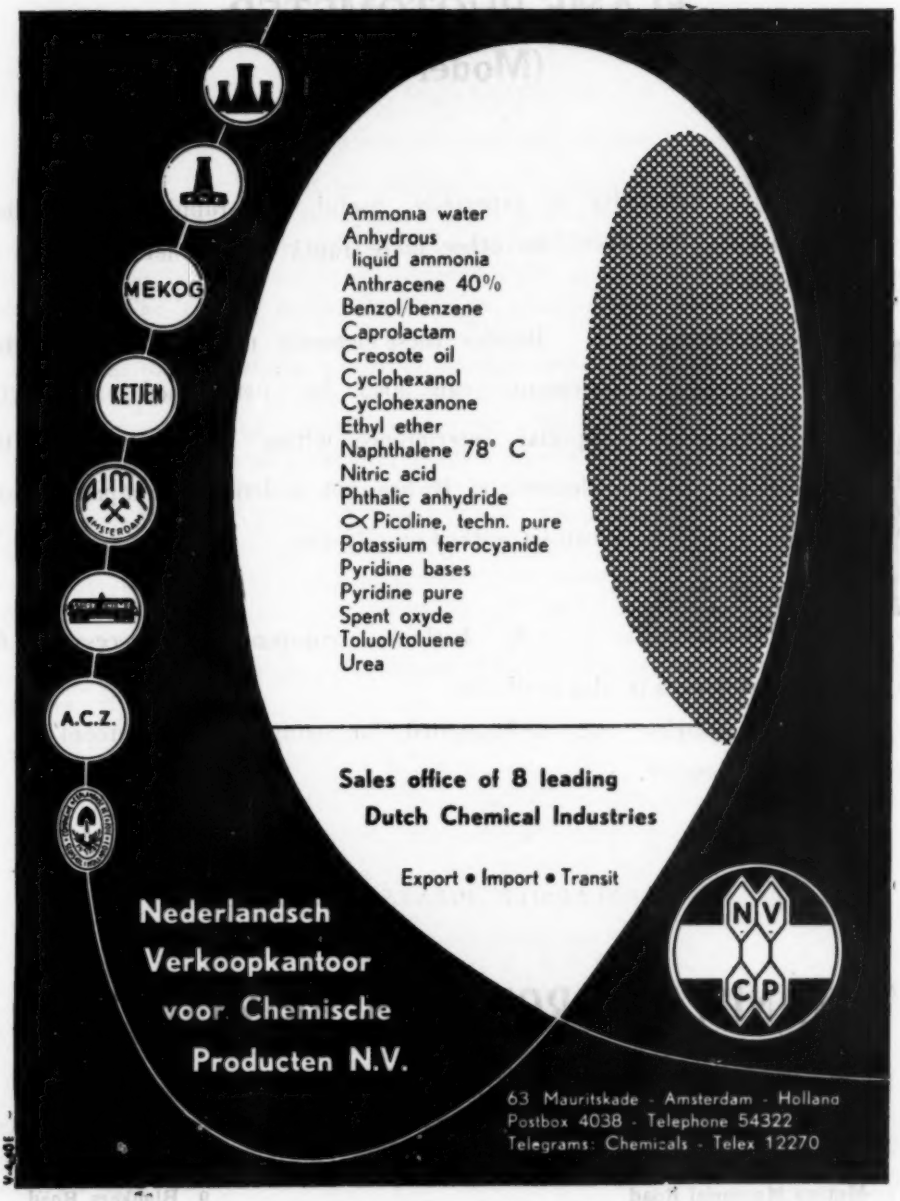
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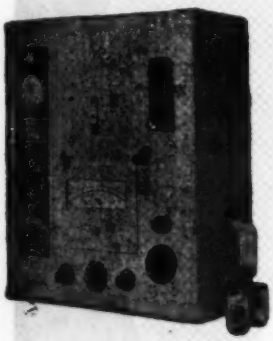

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[Jour. Indian Chem. Soc., Vol. 33, No. 6, 1956]

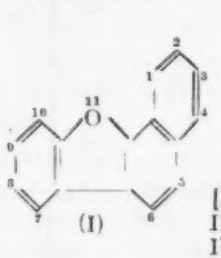
EXPERIMENTS ON THE SYNTHESES OF FURANO COMPOUNDS. PART VIII. SYNTHESIS OF 3:4-BENZODIPHENYLENE OXIDE

By J. N. Chatterjea

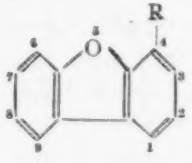
A synthesis of 3:4-benzodiphenylene oxide from 4-dibenzofuryl-lithium is described.

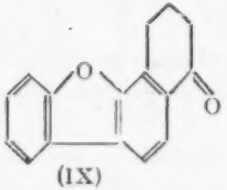
Kruber and Oberkobusch have isolated 3:4-benzodiphenylene oxide (I) (α-brazan, benzo [b] naphtho [2.1-d] furan, also known as 1:2-benzodiphenylene oxide) from coal-tar distillation products (*Chem. Ber.*, 1951, **84**, 831). The constitution of the compound was based on oxidative degradation to 2-phenylcoumarone and related products. The present paper describes an unambiguous synthesis of (I) from diphenylene oxide.

One of the remarkable properties of diphenylene oxide is that in replacement reactions, the position of the entering group is largely determined by the nature of the reactant and *not* by any orienting group. Thus, halogenation, sulphonation or succinoylation occurs in the position-2; nitration introduces a group in the position-3, whilst metalation with mercuric acetate or lithium alkyls proceeds in the position-4 (Gilman and Young, *J. Amer. Chem. Soc.*, 1934, **56**, 1415; Gilman and Morton, "Organic Reactions", Vol. VIII, Wiley, New York, p., 259; Willis, *Chem. Abs.*, 1944, **38**, 739). The metalation proceeds very satisfactorily with *n*-butyl-lithium affording (II) (Willis, *loc. cit.*) and as by appropriate treatment the lithium atom may be replaced by a variety of groups, it is of interest to introduce a butyric acid residue at the position-4 so as to obtain (VIII), which may lead to an unambiguous synthesis of α-brazan (I).



(I)





(IX)

[II: R = Li;
III: R = 4-dibenzofuroyl;
IV: R = CHO; V: R = COOH;
VI: R = CH = CH.COOH;
VII: R = $CH_2.CH_2.COOH$;
VIII: R = $CH_2.CH_2.CH_2.COOH$]

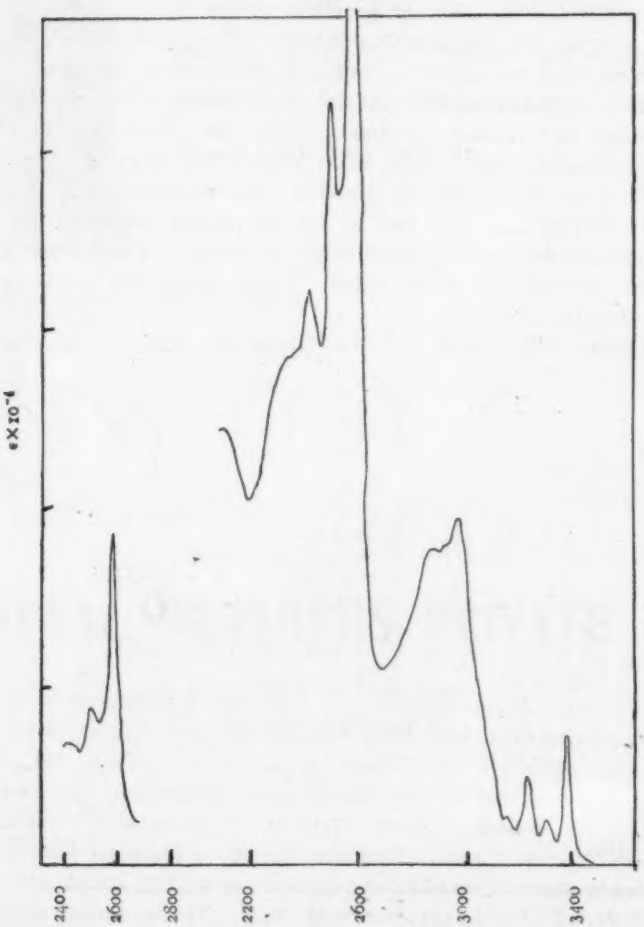
Carbonation of 4-dibenzofuryl-lithium (II) with carbon dioxide at 0° led to the exclusive formation of di-4-dibenzofuryl ketone (III) and the expected acid (V) was not formed even in traces (cf. Gilman *et al.*, *J. Amer. Chem. Soc.*, 1933, **55**, 1258; 1939, **61**, 643). Interaction of (II) and N-methylformanilide furnished the 4-formyl derivative (IV) (cf. Wittig, "Newer Methods of Preparative Organic Chemistry", Interscience, N.Y. 1948, p. 579). This aldehyde on condensation with malonic acid in pyridine (aided by piperidine) yielded the cinnamic acid (VI), which on reduction with sodium amalgam afforded the propionic acid (VII). The orientation of these compounds

was established by oxidation of the acid (VI) with alkaline potassium permanganate to the known dibenzofuran-4-carboxylic acid (V) (Gilman and Young, *loc. cit.*). Homologation of (VII) by the Arndt-Eistert procedure afforded the butyric acid (VIII), isolated by way of the methyl ester. Cyclisation of the acid (VIII) with sulphuric acid or better by polyphosphoric acid proceeded satisfactorily, furnishing the cyclic ketone (IX). Reduction of the latter with lithium aluminium hydride yielded the corresponding carbinol which underwent dehydration and dehydrogenation with palladised charcoal, yielding α-brazan (I), identical with an authentic specimen, very generously supplied by Dr. O. Kruber. The compound has been characterised by a well crystalline picrate.

The U.V. absorption curve of (I) is shown in Fig. 1.

FIG. 1

α-Brazan.



A synthesis of (I) from 2-phenylcoumarone-3-carboxylic acid (cf. Part VI, this *Journal*, 1956, **33**, 175) will be shortly communicated.

EXPERIMENTAL*

4-Formyldibenzofuran.—A mixture of dibenzofuran (8.5 g.) and *n*-butyl-lithium (0.05 mole) in ether was stirred at the room temperature for 12 hours in a current of purified dry nitrogen. An ethereal solution of N-methylformanilide (6.7 g.) was added dropwise to the mixture when a vigorous reaction took place. After leaving the mixture overnight, it was poured into an excess of dilute H_2SO_4. The ethereal layer was separated, dried (sodium sulphate) and the solvent removed, affording the crude aldehyde, mixed with dibenzofuran. This was used in the next operation without purification.

The 2:4-*dinitrophenylhydrazone* crystallised from a large volume of acetic acid in orange-yellow needles, m.p. 305°. (Found: N, 11.7. $C_{19}H_{12}O_5N_4$ requires N, 14.8 per cent).

Di-4-dibenzofuryl Ketone (III).—When CO_2 was bubbled into 4-dibenzofuryl-lithium, obtained above, at 0°, the product was a mixture of unchanged dibenzofuran and the ketone (III). Extraction with alkali did not reveal the presence of any acidic material. The ketone crystallised from alcohol in silky needles, m.p. 174°. Gilman *et al.* (*J. Amer. Chem. Soc.*, 1939, **61**, 643) report m.p. 172-73°. (Found: C, 82.5; H, 4.0. Calc. for $C_{25}H_{14}O_3$: C, 82.8; H, 3.9 per cent). The compound develops a yellow colour with H_2SO_4.

The 2:4-*dinitrophenylhydrazone* was very sparingly soluble in alcohol or acetic acid. It crystallised from nitrobenzene-alcohol in orange-yellow needles, m.p. > 320°. (Found: N, 10.6. $C_{31}H_{18}O_6N_4$ requires N, 10.3 per cent).

The *oxime*, prepared in pyridine, crystallised from alcohol in colorless needles, m.p. 253° (decomp.). (Found: C, 79.2; H, 4.4. $C_{25}H_{15}O_3N$ requires C, 79.5; H, 4.0 per cent).

β-4-Dibenzofurylacrylic Acid (VI).—A mixture of the crude aldehyde (6 g.), malonic acid (10 g.), pyridine (30 c.c.) and piperidine (1 c.c.) was heated on a boiling water-bath for 3 hours. The mixture was diluted, basified with NaOH and the volatile materials removed in a current of steam. The residual alkaline solution was freed from neutral matter by extraction with benzene and then acidified to yield (VI), crystallising from alcohol in colorless plates, m.p. 228°, yield 2.6 g. (Found: C, 75.5; H, 4.0. $C_{15}H_{10}O_3$ requires C, 75.7; H, 4.2 per cent).

4-Dibenzofuryl Carboxylic Acid.—The foregoing acid (VI, 0.3 g.) was dissolved in alkali and boiled for a few minutes with a solution of $KMnO_4$ (0.6 g.) in water (15 c.c.). The mixture was clarified with SO_2 and acidified to furnish the acid (V), crystallising from aqueous alcohol in colorless needles, m.p. 209-10°. Gilman and Young (*loc. cit.*) record m.p. 209°. (Found: C, 73.6; H, 3.8. Calc. for $C_{13}H_8O_3$: C, 73.6; H, 3.7 per cent).

* All m.p.'s are uncorrecetd.

β-4-Dibenzofurylpropionic Acid (VII).—The acid (VI, 2.3 g.) was dissolved in dilute NaOH solution and reduced with sodium amalgam (100 g., 2%) which was added in small portions. After 3 hours the alkaline solution was clarified with charcoal, filtered and acidified, affording the *acid* (VII) as a colorless, crystalline mass, crystallising from alcohol (90%) in long blades, m.p. 148°, yield 2.0 g. (Found : C, 75.5 ; H, 5.0. $C_{15}H_{12}O_3$ requires C, 75.0 ; H, 5.0 per cent).

The *methyl ester*, prepared by diazomethane, was obtained as colorless crystals, m.p. 22-23°.

γ-4-Dibenzofurylbutyric Acid (VIII).—The above propionic acid (1.8 g.) was dissolved in benzene (6 c.c.), treated with purified thionyl chloride (2 c.c.) and a drop of pyridine, and left for 3 hours. On removal of the volatile matter in vacuum on a water-bath, the acid chloride was obtained as a liquid mixed with pyridine hydrochloride. The acid chloride was taken up in benzene (6 c.c.) and added dropwise to a cooled ethereal solution of diazomethane (from nitrosomethylurea, 5 g.) and the mixture left overnight. On removing the solvent in vacuum, the diazoketone was obtained as a crystalline solid which was dissolved in dry methyl alcohol (30 c.c.), warmed to 60° and treated with silver oxide (prepared from $AgNO_3$ soln., 5 c.c., 10%) in small portions. The mixture was refluxed for 12 hours, treated with an additional silver oxide and refluxed for further 2 hours. The mixture was filtered with charcoal, concentrated and the residual oily methyl ester of (VIII) hydrolysed by boiling with alcoholic sodium hydroxide (15 c.c., 10%). On acidification, the *butyric acid* (VIII) was obtained as a gum which slowly solidified ; yield 0.7 g. It crystallised from petroleum ether in colorless crystalline prismatic mass, m.p. 89-90°. (Found : C, 75.5 ; H, 5.5. $C_{16}H_{14}O_3$ requires C, 75.6 ; H, 5.5 per cent).

4-Keto-1:2:3:4-tetrahydro-α-brazan (IX).—The above acid (0.1 g.) was warmed at 175°-180° with polyphosphoric acid derived from phosphoric acid (5 g., 85%) and phosphoric anhydride (2 g.) for 45 minutes. The mixture was treated with ice, extracted with ether, washed with dilute alkali, dried and the solvent removed. The crystalline solid (IX) (70 mg.) crystallised from alcohol in colorless needles, m.p. 148-49°. (Found : C, 81.0 ; H, 5.2. $C_{16}H_{12}O_2$ requires C, 81.4 ; H, 5.1 per cent).

The ketone can also be obtained in presence of sulphuric acid (89%) at the room temperature for 18 minutes and then working up the product as usual.

The 2 :*4-dinitrophenylhydrazone* crystallised from acetic acid in orange needles, m.p. >305°. (Found : N, 13.0. $C_{22}H_{16}O_5N_4$ requires N, 13.5 per cent).

α-Brazan.—A solution of the above ketone (50 mg.) in dry ether (15 c.c.) was treated in cold with a slurry of lithium aluminium hydride (40 mg.) in ether (5 c.c.). After the vigorous reaction was over, the mixture was decomposed after 1 hour with iced HCl, the ethereal extract dried and the solvent removed, furnishing the corresponding alcohol (IX : -CHOH- in place of -CO-) in quantitative yield, m.p. 132°. It was mixed thoroughly with palladised charcoal (0.5 g.) (Linstead and Thomas, *J. Chem. Soc.*, 1940, 1127) and heated in a metal bath at 280°-310° for 2 hours. The characteristic odour of α-brazan was perceptible. The mass was extracted with benzene, filtered through a column of alumina, concentrated and the residue (28 mg.) was obtained as colorless needles, m.p. 102-103°, undepressed on admixture with an

authentic specimen. (Found: C, 88.5; H, 4.2. Calc. for $C_{16}H_{10}O$: C, 88.1; H, 4.5 per cent).

U. V. absorption: λ_{max} (in absolute alcohol), 3380 Å ($\epsilon=7450$), 3305 Å ($\epsilon=2640$), 3230 Å ($\epsilon=5050$), 3160 Å ($\epsilon=2720$), 2970 Å ($\epsilon=19500$), 2880 Å ($\epsilon=17900$), 2590Å ($\epsilon=94100$), 2495 Å ($\epsilon=43100$), 2410 Å ($\epsilon=32400$) and 2100 Å ($\epsilon=24800$).

α-Brazan gave an orange-red picrate from alcoholic picric acid, m.p. 109-10°. (Found: C, 59.6; H, 3.0. $C_{16}H_{10}O.C_6H_3O_7N_3$ requires C, 59.1; H, 2.9 per cent).

The author wishes to thank Dr. O. Kruber for the provision of a specimen α-brazan obtained from coal tar.

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Received August 26, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 6, 1956]

ON THE CONSTITUTION OF SERPININE, A MINOR ALKALOID OF *RAUWOLFIA SERPENTINA* BENTH. *

By S. Bose

From *R. serpentina* Benth. a new alkaloid, serpinine, $C_{20}H_{24}ON_2$, has been isolated in poor yield. Its colour reactions, properties, U. V. and I. R. spectra have been examined. Several degradative experiments have been carried out. From the available experimental data, a hexahydro-β-carboline structure of serpinine has been suggested. It is found to be closely related to ajmaline in properties and constitution.

The occurrence of a new alkaloid, serpinine, as a minor base in the root of Dehra Dun variety of *Rauwolfia serpentina* Benth. was reported earlier by the present author (*Naturwiss.*, 1955, **42**, 71). The base has now been isolated in sufficient quantity for studying its properties and chemical constitution, a detailed account of which is presented in this communication.

Serpinine, $C_{20}H_{24}ON_2$, has been isolated from the accumulated mother-liquor of rauwolfinine (Bose, this *Journal*, 1954, **31**, 47). It crystallises from alcohol in glistening rectangular plates which melt at 315-17° with simultaneous decomposition and sublimation. Serpinine does not possess any methoxyl group but it contains one N-Me and one C-Me function. It feebly reduces Tollen's reagent and is not soluble in aqueous sodium hydroxide. Serpinine does not produce any characteristic coloration with ferric chloride, but it responds to the following colour reactions with various alkaloidal reagents (Table I).

TABLE I

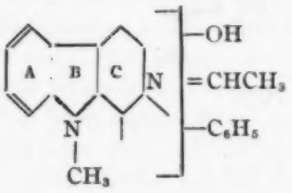
Reagents.	Colour.	Reagents.	Colour.
1. Conc. H_2SO_4	Nil	5. Ehrlich	Brown
2. Fröhde's	Nil	6. Hopkins-Cole	Slight brown
3. Otto	No charateristic colour	7. Conc. HNO_3	Deep red
4. Keller	Do	8. Ceric sulphate + conc. H_2SO_4	Bright red

These colour reactions indicate the presence of an indoline moiety in the base which has received independent confirmation from the studies of its ultraviolet and infra-red absorption spectra.

* Since submission of this paper, a manuscript on "The Structures of Tetraphyllicine, Ajmalidine and Rauvomitine" has been received from Dr. C. Djerassi of Wayne University, Michigan, U.S.A. The constitution of tetraphyllicine appears to be identical with serpinine.

The U.V. curve of serpinine, which has been studied in ethanol with a Beckman quartz spectrophotometer (Model DU), resembles very closely those of indoline bases, namely, ajmaline (Chatterjee and Bose, this *Journal*, 1954, **31**, 17) and rauwolfinine (Bose, *ibid.*, 1954, **31**, 311). It shows λ_{max} at 250mμ (log ε, 3.97) and 293 mμ (log ε, 3.51), and λ_{min} at 227 and 272 mμ respectively. The infra-red spectrum of serpinine, examined in nujol mull with a Baird double-beam spectrophotometer, exhibits absorption bands at 6.25μ (indoline nucleus), 6.84μ (phenyl nucleus), 7.24μ (C-Me), 7.4μ (N-Me) and 13.55μ (*o*-disubstituted phenyl) besides two other bands at 2.85μ (weak) (for -OH group) and at 11.2μ (attributable to an exocyclic double bond). Serpinine, when treated with *p*-toluenesulphonyl chloride and pyridine, forms a crystalline monotosyl derivative, m.p. 191-92°. The base does not form any oxime and is not changed by sodium borohydride. Upon ozonolysis it forms acetaldehyde, which has been identified as its *p*-nitrophenylhydrazone, m.p. 125-26°. The isolation of acetaldehyde confirms the presence of an exocyclic ethylidene group which is discernible in the I.R. spectrum of the base.

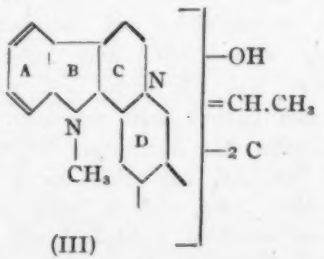
For determining the skeletal structure of the alkaloid, it has been subjected to selenium dehydrogenation at 300°. From the degradation products several uncharacterised indolaceous compounds have been obtained besides Ind-N-methylharman, which has been identified as its picrate, $C_{19}H_{15}O_7N_5$, m.p. 260-61° (decomp.). The isolation of Ind-N-methylharman has induced the author to suggest the following partial structure (I) for serpinine:



(I)

(II)

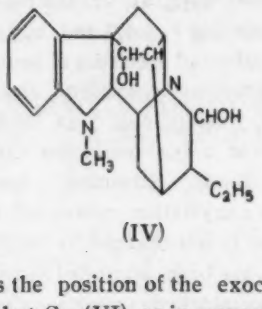
Now all *Rauwolfia* alkaloids, partial or total structure of which is known, are at least tetracyclic (II). Serpinine, which belongs to this group of alkaloids, is likely to possess similar fused ring system (III) by analogy.



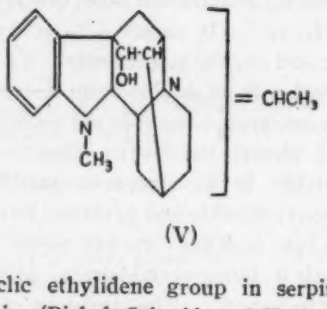
(III)

Further evolution of the structure (V) for serpinine has been possible by the application of Woodward's fission hypothesis (*Nature*, 1948, **162**, 155) and the theory

(*Angew. Chem.*, 1956, **68**, 13) that he has developed for deducing unambiguously the structure of ajmaline (IV), a companion of serpinine.

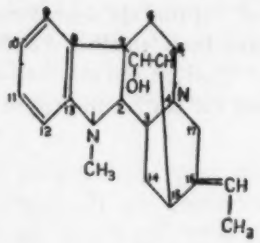


(IV)



(V)

As regards the position of the exocyclic ethylidene group in serpinine, it is most probably located at C_{16} (VI), as in mavacurine (Bickel, Schmidt and Karrer, *Helv. Chim. Acta*, 1955, **38**, 649), corresponding to the ethyl group in ajmaline.



(VI)

EXPERIMENTAL

Isolation of Serpinine.—Crude rauwolfinine (20.0 g.), isolated from the alcoholic extract of the roots of *R. serpentina* Benth. of Dehra Dun variety by the process described earlier (Bose, *loc. cit.*, p. 47), was purified by crystallisation from alcohol. The mother-liquor, obtained after separation of the crystals of rauwolfinine, was concentrated to a small volume and kept in a frigidaire. After some time it was found that needle-shaped crystals were deposited along with a gummy mass. The crystals, m.p. 305-10° (with decomposition and sublimation) were freed from the adhered gum by washing with alcohol, and collected. The alcoholic filtrate was concentrated and poured into 1% acetic acid solution (100 c.c.) and kept overnight, when a dark brown gummy mass separated. It was filtered off and the filtrate was cooled and basified with ammonium hydroxide. The brownish white flocculent precipitate, thus obtained, was taken up in ether (300 c.c.). The ether extract was washed with water, dried, and on being concentrated, left a brownish semi-solid residue. This was dissolved in alcohol and the concentrated solution was seeded with a crystal obtained beforehand, when fine needles, m.p. 304-10° (with decomposition and sublimation), were deposited. They were mixed with crystals obtained earlier and the whole lot was crystallised thrice from absolute alcohol,

when serpinine crystallised out in glistening rectangular plates, m.p. 315-17° (with simultaneous decomposition and sublimation), yield 0.55 g. [Found (in a sample dried in vacuo over P_2O_5 at 140° for five hours): C, 77.74, 77.85; H, 7.66, 7.70; N, 8.93, 8.98; N.Me, 4.78; C.Me, 4.31; eq. wt. (conductometric titration), 305. $C_{20}H_{24}ON_2$ requires C, 77.91; H, 7.79; N, 9.09; 1N.Me, 4.87; 1C.Me, 4.87 per cent. Eq.wt., 308]. Serpinine is moderately soluble in methanol, ethanol and ethyl acetate and is sparingly soluble in chloroform, benzene and ether. It produces an orange-red precipitate with potassium bismuth iodide and a yellowish white precipitate with potassium mercuri-iodide.

Preparation of Monotosyl Derivative of Serpinine.—A solution of well-dried serpinine (0.05 g.) in dry pyridine (3 c.c.) was added to a solution of *p*-toluene-sulphonyl chloride (0.05 g. dissolved in 2 c.c. of dry pyridine) at 0°. The mixture was kept at room temperature for a week and afterwards heated on steam-bath for 4 hours. It was next poured into ice-cold sodium bicarbonate solution (20 c.c.) and extracted with chloroform (60 c.c.). The chloroform extract was washed with water, dried and distilled to leave a solid residue. This was mixed with dry benzene and the benzene distilled off under reduced pressure to remove last traces of pyridine. The residue, thus obtained, was crystallised from alcohol, when crystals of serpinine monotosylate, m.p. 191-92°, were deposited. (Found in a sample dried in vacuo over P_2O_5 at 100° for 4 hours: N, 5.92. $C_{27}H_{30}O_3N_2S$ requires N, 6.06 per cent).

Ozonolysis of Serpinine.—Ozonolysis of serpinine (0.15 g.) was carried out by following the same method as adopted by Karrer in the case of mavacurine and fluoro-curine (Bickel, Schmidt and Karrer, *loc. cit.*). The acetaldehyde vapour liberated from the ozonolysis products of serpinine was directly passed into an ice-cold 5% aqueous solution of *p*-nitrophenylhydrazine hydrochloride. The precipitate formed was filtered, washed with water and dried. The dry mass was crystallised from aqueous alcohol when yellow needles were obtained, m.p. 125-26°. (Found in a sample dried in vacuo over P_2O_5 at 70° for 4 hours: N, 23.2. Calc. for $C_8H_9O_2N_3$: N, 23.46 per cent). It did not depress the m.p. of an authentic sample of acetaldehyde-*p*-nitrophenylhydrazone, when mixed.

Selenium Dehydrogenation of Serpinine at 300°.—A thoroughly powdered mixture of serpinine (0.25 g.) and black selenium (0.25 g.) was taken in a hard glass tube and heated up very quickly to 300° in a metal bath, when a vigorous reaction set in. Heating was continued at 300° for five minutes more. The test tube was next allowed to cool and powdered with fine sand, and the mixture was extracted with benzene in a Soxhlet for 6 hours. The dark benzene extract was filtered through a kieselguhr bed and the clear filtrate was evaporated to leave an oily residue. This on distillation in high vacuum yielded a yellow oil, b.p. 80°-130°/0.01 mm. together with red selenium. The oil was taken up in ether (50 c.c.) and shaken with 5% aqueous hydrochloric acid (60 c.c.) when two fractions, (A) and (B), were obtained. The ether layer (B) containing non-basic products left an oily residue on removal of the solvent. From the faecal odour of the oil and also from its positive Ehrlich and pine chip test, it is suggested that the oily residue is a mixture of several uncharacterised indole compounds. The aqueous acid fraction (A) was cooled in ice and basified with

NaOH and thoroughly extracted with ether. The ether extract (200 c.c.) was washed with water, dried and concentrated to leave a small amount of an oily residue. This on high vacuum sublimation yielded a few drops of a pale yellow oil, b.p. 110°-120°/0.01 mm. The oil did not solidify on keeping. It was next converted into picrate by mixing its ethereal solution with an ethereal solution of picric acid. The crude picrate was crystallised twice from absolute ethanol in which it was sparingly soluble. The pure picrate melted at 260-61° with decomposition and did not show any depression in m.p. when mixed with an authentic sample of Ind-N-methyl-harman picrate. [Found (in a sample dried in vacuo over P_2O_5 for 5 hours at 140°): C, 53.54; H, 3.49; N, 16.41. Calc. for $C_{12}H_{12}N_2.C_6H_2(NO_2)_3OH$: C, 53.65; H, 3.53; N, 16.47 per cent].

The author takes this opportunity to offer his sincere thanks to Dr. (Mrs.) A. Chatterjee, Reader in the Department of Chemistry, for the laboratory facilities provided.

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Received February 2, 1956.

[Jour. Indian Chem. Soc., Vol. 33, No. 6, 1956]

THE ALKALOIDS OF *RAUWOLFIA BEDDOMEI* HOOK. F. PART I

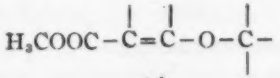
By S. Bose, S. K. Talapatra and (Mrs.) A. Chatterjee

δ-Yohimbine and sarpagine have been isolated from the roots of *Rauwolfia beddomei* Hook.

In connection with our investigations on *Rauwolfia* species, it appeared of interest to examine *Rauwolfia beddomei* Hook, a plant indigenous to South India. This study seemed especially pertinent because of the report (Pillay, Rao and Rao, *Ind. J. Pharm.*, 1955, **17**, 91) that the roots of *R. beddomei* contain several alkaloids as revealed from their paper chromatographic examination.

Through the courtesy of Messrs. Rajaranga & Co., Ltd., Madras, some quantity of authentic *R. beddomei* roots has been obtained and a brief study of the alkaloids present in its root-bark is reported herein.

Alkaloids were drained from the powdered roots by cold percolation with ethyl alcohol. Chromatographic resolution of a benzene solution of this crude base (yield 0.022%) over Merck's alumina furnished an alkaloid, $C_{21}H_{24}O_3N_2$, m.p. 257° (decomp.) (approx. 27% of the total base). It crystallises from ethyl alcohol in prisms containing a molecule of alcohol as solvent of crystallisation. The alkaloid does not produce any characteristic coloration with ferric chloride and is free from :$N.CH_3$, hydroxyl and methylenedioxy groups. It possesses a side methyl and methoxyl function. It has $[\alpha]_D^{28} = -62.18°$ (chloroform). Its monoacidic character is indicated by conductometric titration and it readily forms a monohydrochloride, $C_{21}H_{24}O_3N_2.HCl$, m.p. 290° (decomp.). From infra-red (peak absorption at 5.87 and 6.16μ) and ultraviolet data (increased absorption at 250 mμ) of this alkaloid, the existence of a β-alkoxy-acrylic ester group (I) (Chatterjee and Talapatra, *Science & Culture*, 1955, **20**, 568) has been concluded.



(I)

The infra-red spectrum also exhibits bands at 2.85μ (>NH), 7.25μ ( ) and 9.05μ (ether bridge).

The alkaloid has been shown to be a tetrahydro-β-carboline derivative from evidence of colour reactions (Rossi, Boca and Lobo, *Anal. farm. bioquim.*, 1932, **3**, 51). It was, in fact, proved to be identical with δ-yohimbine (Chatterjee and Talapatra, *loc. cit.*) by direct comparison of their m. p., properties, ultraviolet and infra-red spectra (Table I) as also of their paper chomatograms.

TABLE I

	δ-Yohimbine from *R. beddomei*.	δ-Yohimbine from *R. serpentina*. *
Melting point	257-58° (decomp.)	257° (decomp.).
Mol. formula	$C_{21}H_{24}O_3N_2$	$C_{21}H_{24}O_3N_2$
Optical rotation	$[\alpha]_D^{25} = -62.18°$ ($CHCl_3$)	$[\alpha]_D^{30} = 60° (\pm 2°)$ ($CHCl_3$)
Solubility	Sparingly soluble in ethanol and methanol; highly soluble in chloroform and pyridine.	Sparingly soluble in ethanol and methanol.
Crystalline form	Prismatic needles from ethanol with one molecule of solvent of crystallisation.	Prisms from ethanol.
U.V. spectrum in ethanol	Maxima at 225, 281 and 292 mμ and increased absorption at 250 mμ.	Maxima at 225 and 283 mμ with strong absorption at 250 mμ.
I.R. spectrum (characteristic bands at)	2.85, 5.87, 6.16 and 9.05 μ	3.1, 5.88, 6 20 and 9.0 μ.
Mol. formula and m.p. of hydrochloride	$C_{21}H_{24}O_3N_2$. HCl, 290° (decomp.)	$C_{21}H_{24}O_3N_2$, HCl, 280-90° (decomp.)

* Hofmann, *Helv. Chim. Acta*, 1954, **37**, 849.

Another base, $C_{19}H_{22}O_2N_2$, m.p. 364-66° (decomp.), was obtained from the basic resin (vide Experimental) in very poor yield (0.0007%) by employing chromatography technique. It is readily soluble in alkali and reduces Fehling's and ammoniacal silver solutions. It is free from methylenedioxy : $N.CH_3$, methoxy and carbonyl (ketonic, aldehydic or lactonic) functions. The alkaloid exhibits the following colour reactions which are characteristics of a tetrahydro-β-carboline derivative (Table II).

TABLE II

Reagent.	Colour.	Remarks.
$FeCl_3$	Red with pink tinge.	Deepens on keeping.
1% Ceric sulphate in 2*N*-H_2SO_4	Violet.	Persists for a long time.
Fröhde's reagent	Immediate navy-blue.	Changes to green.
Conc. H_2SO_4+$K_2Cr_2O_7$	Navy-blue.	Fades to yellow.
Glyoxal sodium bisulphite+conc. H_2SO_4	Blue with violet tinge.	Gradually acquires greenish tinge.
$FeCl_3$ + glacial acetic acid + conc. H_2SO_4 (Keller's reaction)	Light violet.	Persists.

From its properties, melting point and colour reactions (Table III), this alkaloid is shown to be identical with sarpagine, $C_{19}H_{22}O_2N_2$, which has been found to occur in various *Rauwolfia* species, viz., *R. canescens* L. (Keck, *Naturwiss.*, 1955, **42**, 391; Bhattacharji, Dhar and Dhar, *J. Sci. Ind. Res.*, 1955, **14B**, 310), *R. serpentina* Benth. (Stoll and Hofmann, *Helv. Chim. Acta*, 1953, **36**, 1143; Thomas, *Chem. & Ind.*, 1954, 488; Bodendorf and Eder, *Naturwiss.*, 1953, **40**, 342; *Ber.*, 1954, **87**, 818), *R. heterophylla* Roem ex Schult (Hochstein, Murai, Boegemann, *J. Amer. Chem. Soc.*, 1955, **77**, 351), *R. indecora* R.E. Woodson (Ishidate, Okada and Saito, *Bull. Soc. Phar., Japan*, 1955, **3**, 319) and *R. hirsuta* Jacq. (Vergara, *J. Amer. Chem. Soc.*, 1955, **77**, 1864). Further work on sarpagine is in progress.

TABLE III

	Sarpagine from *R. beddomei*.	Sarpagine from *R. serpentina*. *
Melting point	Sinters and turns brown above 320°; melts at 364-65° with decomposition.	Sinters and turns brown above 320°; melts at 363-64° with decomposition.
Molecular formula	$C_{19}H_{22}O_2N_2$	$C_{19}H_{22}O_2N_2$
Solubility	Moderately soluble in boiling ethanol, less soluble in boiling methanol and least so in acetone; insoluble in chloroform, ether and petroleum ether.	Soluble in 60 parts boiling ethanol, 250 parts methanol, and about 400 parts acetone; insoluble in chloroform, ether and petroleum ether.
Crystalline form	Fine needles with one molecule of ethanol of crystallisation.	Fine needles with one molecule of ethanol of crystallisation.
NaOH solution	Dissolves.	Dissolves.
Tollen's reagent	Reduced.	Reduced.
Fehling's solution	Do	Do.
Keller's reagent	Violet colour.	Violet colour.
$FeCl_3$ solution	Red with pink tinge.	Pink.

* Stoll and Hofmann, *Helv. Chim. Acta*, 1953, **36**, 1143.

EXPERIMENTAL

Dried powdered roots (8.0 kg.) of *Rauwolfia beddomei* were extracted with 95% alcohol (18 litres) containing 0.1% acetic acid in a percolator for a week. The reddish brown alcoholic extract was concentrated under reduced pressure on a water-bath to about 200 c.c. The thick deep brown extract was poured into cold water (1.5 litres) containing 1% acetic acid in a thin stream, kept overnight in a refrigerator, and filtered from the separated non-basic resinous mass through a celite bed. The resin was washed several times with 1% acetic acid. The combined filtrates were cooled, extracted with ether (300 c.c. each in 3 instalments) to remove ether-soluble impurities. The aqueous solution was then cooled, covered with 400 c.c. ether and treated with ammonia to p_H 8-8.5, when an ether-insoluble basic gum (A) separated. This was removed.

The ethereal portion was separated and the aqueous layer was extracted several times with ether (2 litres in all in 4 instalments). The combined ether extract (showing violet fluorescence) was washed with water, dried over anhydrous sodium sulphate, and concentrated when a gummy residue was obtained which failed to crystallise from organic solvents or their mixtures. It was dissolved in acetone (about 60 c.c.) and the resulting deep brown solution was chromatographed through a column of alumina (38 cm. × 2.5 cm.). The chromatogram was eluted with benzene and other solvents. Eluates were collected in fractions of 30 c.c. (Table IV).

TABLE IV

Chromatography of the crude ether-soluble base of R. beddomei.

Eluents.	Fractions.	Residue on evaporation.
Benzene	1	0·56 g. Crystallises from alcohol, m.p. 252-53° (dec.)
Do	2-5	0·6 g. Do
Do	6-7	Nil
Benzene + 50% acetone	8-9	0.3 g. Gummy, uncrystallisable
Do	10	Nil
Acetone	11-12	0.2 g. Uncrystallisable
Do	13	Nil
Alcohol	14	Nil
Chloroform	15-16	0.05 g. Uncrystallisable.

Fractions (1-5) crystallised from alcohol in prisms (yield 0.55 g.), m.p. 252-54° (decomp.). The purification of the base (for analytical purpose) was done by several recrystallisations from methanol and from ethanol, when shining prismatic needles, m.p. 257-58° (decomp.), were obtained. It is sparingly soluble in methanol, ethanol and benzene, fairly in acetone, readily in pyridine and chloroform and insoluble in light petroleum ether and water. The alkaloid (0.42 g.), crystallised from ethanol, lost 0.0487 g. in weight when dried at 140° for 16 hours in vacuo over P_2O_5 and the shining transparent crystals turned opaque. The crystals had the approximate composition: $C_{21}H_{24}O_3N_2$, C_2H_5OH.

0.402 g. of the substance in 10 c.c. chloroform showed a rotation of -2.5° in 1 d.cm. tube at 25°, whence $[\alpha]_D^{25} = -62.18°$. [Found in a dry sample: C, 71.87; H, 7.05; N, 8.00; OMe, 0.82; :C.Me, 4.01; M. W., 356.3 (potentiometric titration; 0.1005 g. of the base consumed 2.82 c.c. of 0.1 N-HCl). Calc. for $C_{21}H_{24}O_3N_2$: C, 71.59; H, 6.81; N, 7.95; OMe, 8.80; :C.Me, 4.26 per cent. M.W., 352].

The alkaloid did not show any depression in m.p. when admixed with an authentic sample of δ-yohimbine.

Hydrochloride of the Base (δ-*Yohimbine*).—The base (0.1 g.) was dissolved in hot aqueous HCl (2*N*, 5 c.c.) and the solution upon cooling produced δ-yohimbine hydrochloride (0.095 g.). It crystallised from water in fine leaflets, m.p. 290° (decomp). [Found in a dry specimen: C, 64.64; H, 6.42; N, 7.23; Cl, 9.46. Calc. for $C_{21}H_{24}O_3N_2$, HCl: C, 64.86; H, 6.43; N, 7.20; Cl, 9.13 per cent].

Isolation of Sarpagine from R. beddomei *Hook.*—The basic gum (A) (*vide supra*) was dried, mixed with an equal amount of sand and soxhletted for 16 hours with acetone. The acetone extract was concentrated to about 50 c.c., cooled and chromatographed through a column of alumina (45 cm. × 2.5 cm.) using benzene and other solvents as eluents. Eluates were collected in fractions (30 c.c. each) (Table V).

TABLE V

Eluents.	Fraction.	Residue on evaporation.
Benzene	1 : Dark reddish brown solution with green fluorescence.	Gummy.
Do	2 : Same.	Gummy.
Do	3 : Reddish yellow solution with strong green fluorescence.	Needle-shaped crystals m.p. 362° (decomp.).
Do	4	Little residue, few crystals, m.p. 362° (decomp.).
Do	5	Nil
Benzene+50% acetone	6-7	Trace of uncrystallisable residue
Acetone	8-9	Same
Chloroform	10	Same.

Fractions 3 and 4, when triturated with methanol, deposited fine silky needles, m.p. 362° (decomp.), (0.06 g.). These were filtered and washed from the adhering gum with ice-cold acetone. Sarpagine, thus obtained, was purified by several crystallisations from ethanol when colorless needles with alcohol of crystallisation, melting at 364-65° (sintering and turning brown above 320°) with decomposition, separated out. The base (38.9 mg.) lost ethanol of crystallisation (5.1 mg.) and turned opaque after complete drying in vacuo over P_2O_5 at 140° for 20 hours. (Found in a dry sample : C, 73.64 ; H, 7.42 ; N, 9.19. $C_{21}H_{22}O_2N_2$ requires C, 73.52 ; H, 7.15 ; N, 9.03 per cent). The base did not show any depression in m.p. when admixed with an authentic sample of sarpagine.

Potentiometric Titration of Sarpagine.—An alcoholic solution of dry sarpagine (19.5 mg.) consumed 0.64 c.c. of 0.1*N*-HCl when titrated potentiometrically, whence mol. wt. = 304.7. $C_{21}H_{22}O_2N_2$ requires M W., 310.

Hydrochloride of Sarpagine.—For the isolation of sarpagine hydrochloride, the solution left after potentiometric titration (*vide supra*) was worked up according to the method of Stoll and Hofmann (*Helv. Chim. Acta*, 1951, **36**, 1143). The hydrochloride crystallised from alcohol in colorless needles which decomposed above 225°. [Found in a dry specimen : C, 65.64 ; H, 6 52 ; N, 8.15 ; Cl, 9.93. $C_{19}H_{22}O_2N_2$, HCl requires C, 65.80 ; H, 6.63 ; N, 8.08 ; Cl, 10.24 per cent].

Fractions 1, 2, 6, 9 (Table V) and fractions 8, 9, 11, 12, 15 and 16 (Table IV) responded to Dragendorff's test for alkaloids, indicating thereby that some other basic components were concealed in these fractions which could not be obtained in crystalline state as yet.

In conclusion the authors wish to acknowledge their grateful thanks to Dr W. Schöniger, Sandoz A. G., Basel, Switzerland, for microanalyses, Dr. A. Stoll, Sandoz A. G., Basel, Switzerland for the generous gift of an authentic sample of sarpagine, to Dr. J. M. Mueller, Ciba Pharma Ltd., Switzerland for I. R. spectrum of δ-yohimbine and to the Council of Scientific and Industrial Research (India) for financial assistance to one of them (S.K.T.).

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Received April 26, 1955

[Jour. Indian Chem. Soc., Vol. 33, No. 6, 1956]

PREPARATION OF SOME THIAZOLE DYES OF DOEBNER VIOLET TYPE

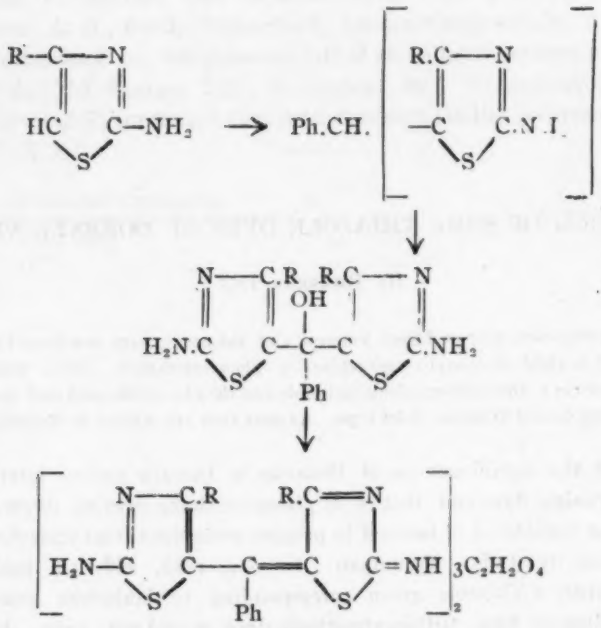
By Bhaskar Das

4-Aryl-2-aminothiazoles, prepared from ketones and thioureas, were condensed with benzaldehyde in presence of HCl to yield di-(4-aryl-2-aminothiazyl-5-)-phenylmethanes. These were oxidised by lead dioxide in acid solution to the corresponding carbinols and then by oxalic acid and ammonium oxalate to the corresponding dyes of Doebner violet type. As dyes they are inferior to Malachite green.

In view of the significant use of thiazoles in therapy and as intermediates in the synthesis of cyanine dyes and that of triphenylmethane dyes as dyestuffs and also in medicine, it was considered of interest to prepare some dyes from thiazoles, analogous to triphenylmethane dyestuffs. Traumann (*Annalen*, 1888, **249**, 50) made unsuccessful attempts to prepare a Thiazole green corresponding to Malachite green or Thiophene green. According to him, trithiazylmethane dyes would not exist, due probably to the absence of *para* position in the azoles. He failed to obtain any dye by joint oxidation of thiazylamines with methylthiazylamine by the action of mercuric chloride. This view was, however, disputed by several workers who regarded the amino group in 2-aminothiazoles, for all practical purposes, as *para* to position-5, basing their argument on the fact that sulphur in cyclic union as equivalent of CH=CH group. That the amino group in 2-position in 2-aminothiazoles activates the carbon atom in position-5 is supported by several experimental facts like coupling or condensation with chlorosulphonic acid (Faith, *J. Amer. Chem. Soc.*, 1947, **69**, 2068).

In support of their assumptions, Bogert and Chertcoff have successfully condensed 2-aminothiazoles with aromatic aldehydes in presence of hydrochloric acid to afford monoaryl-dithiazylmethanes. Such condensations may also be effected with 2-aminothiazoles carrying alkyl groups instead of aryls in position-4, indicating that the above condensations are not dependent on any aryl group in that position and that such a group does not participate in the reaction and that therefore the attachment is at position-5. It appeared to us of interest to verify the observation of Bogert and Chertcoff with 2-amino-4-naphthylthiazole and others in our attempts to prepare some interesting thiazole analogues of triphenylmethane dyes.

In the present work, five different 2-aminothiazoles having different substituents in position-4 have been studied. These were first condensed with benzaldehyde in presence of hydrochloric acid. Di-(4-aryl-2-aminothiazyl-5-)-phenylmethanes were obtained from which the corresponding carbinols and dyes were prepared. The reactions proceed as formulated below :



(R = simple or substituted aryl radical)

The leuco-bases, so obtained, are generally pale yellow or slightly grey in colour ; the carbinols are red-black and the dyes (oxalates) are deep green-black. Comparison of certain properties of these new compounds with those of triphenylmethane derivatives of analogous structure discloses very interesting resemblances. Although of Doebner violet type, in the sense that the thiazole amino groups are unalkylated, these compounds afford green dyestuffs.

The dyeing characteristics of these dyes with respect to cotton are being studied. Study of the substantivity of these to cotton is also proposed to be carried out by the ultraviolet light absorption method.

Experimental

Di-(4-α-naphthyl-2-aminothiazyl-5-)-phenylmethane (I).—A mixture of 4-naphthyl-2-aminothiazole (4.3 g.), benzaldehyde (0.93 g.) and HCl (conc., 10 c.c.) was refluxed for 5 hours at 145°. The mixture was then cooled and basified with NH_4OH. When diluted with water, the leuco-base was precipitated as a fine light yellow powder which was purified by crystallisation from alcohol, m.p. 165° (decomp.), yield 70%. (Found : N, 10.52 ; S, 11.95. $C_{33}H_{24}N_4S_2$ requires N, 10.37 ; S, 11.85 per cent).

Carbinol Base (II) *of* (I).—To a cooled solution of the leuco-base (I, 2.7 g.) in HCl (1.2 g.) and alcohol (100 c. c.) 2 c. c. of 40% acetic acid was added, followed by lead dioxide (1.25 g.) and the mixture was stirred continuously at 5°. After 3 hours, when the oxidation was complete, the mixture was filtered and an excess of ammonium

hydroxide was added to the filtrate. The latter was diluted when a precipitate appeared. This was kept overnight, filtered and crystallised from alcohol, m.p. 140° (decomp.), yield 60%. (Found : S, 11.06. $C_{33}H_{24}ON_4S_2$ requires S, 11.51 per cent).

Oxalate Dye (III) *derived from* (II).—To a solution of (II, 2.4 g.) in 10 c.c. of acetone an aqueous solution of oxalic acid (1.2 g.) and ammonium oxalate (0.12 g.) was added. The colour of the solution changed immediately from brown to green. On evaporating off the acetone the dye was filtered and washed with water. It was purified by crystallisation from dilute alcohol as a dark green powder, m.p 170° (decomp.), yield 60%. (Found : S, 8.92. $C_{66}H_{44}N_8S_4$. $3C_2H_2O_4$ requires S, 9.51 per cent).

Di-(4-p-tolyl-2-aminothiazyl-5-)-phenylmethane (IV) was prepared from 4-*p*-tolyl-2-aminothiazole (3.66 g.), benzaldehyde (0.93 g.) and HCl (conc., 8 c.c.) as in the above case. The product was isolated from the alcoholic solution by dilution with water after basification with NH_4OH and was crystallised from alcohol in greyish yellow powder, m. p. 247° (decomp.), yield 90%. (Found : S, 13.49. $C_{27}H_{24}N_4S_2$ requires S, 13.67 per cent).

Carbinol base (V) was prepared by oxidation of the leuco-base (IV, 2.3 g.) with PbO_2 (1.2 g.) in HCl (1.2 g.), alcohol (100 c.c.) and 40% acetic acid (2 c.c.). The base was isolated as before as a pale brown precipitate when crystallised from alcohol, m.p. 152° (decomp.), yield 85%. (Found : S, 13.02. $C_{27}H_{24}ON_4S_2$ requires S, 13.22 per cent).

Dye (oxalate) (VI) was prepared from (V, 2.1 g.), dissolved in acetone (10 c.c.) by treatment with an aqueous solution of oxalic acid (1.2 g.) and ammonium oxalate (0.12 g.). It was purified by crystallisation from dilute alcohol as a green-black powder, m.p. 149° (decomp.) yield 65%. (Found : S, 11.09. $C_{54}H_{44}N_8S_4$. $3\ C_2H_2O_4$ requires S, 10.64 per cent).

Di-(4-p-chlorophenyl-2-aminothiazyl-5-)-phenylmethane (VII) was prepared from 4-*p*-chlorophenyl-2-aminothiazole (4.1 g.), benzaldehyde (0.93 g.) and HCl (conc., 10 c.c.) and purified by crystallisation from alcohol, as a very light yellow powder, m.p. 172-74° (decomp.), yield 80%. (Found : S, 13.04. $C_{25}H_{18}N_4S_2Cl_2$ requires S, 12.57 per cent).

Carbinol base (VIII) *of* (VII) *and the Dye (oxalate)* (IX).—The leuco-base was oxidised to the carbinol (m.p. 114°, decomp.) by lead dioxide and hydrochloric acid, from which the dye (oxalate) was prepared. The latter was purified by crystallisation from dilute alcohol as a dark green powder which decomposed with swelling above 160°, yield 60%. (Found : S, 10.25. $C_{50}H_{32}N_8S_4Cl_4$. $3C_2H_2O_4$ requires S, 9.96 per cent).

Di-(4-p-methoxyphenyl-2-aminothiazyl-5-)-phenylmethane (X) was prepared from 4-*p*-methoxyphenyl - 2 - aminothiazole (3.8 g.) and benzaldehyde (0.93 g.) as in the previous cases and purified by crystallisation from alcohol as pale greyish yellow small needles, m.p. 196° (decomp.), yield 90%. (Found : S, 12.52. $C_{27}H_{24}O_2N_4S_2$ requires S, 12.80 per cent).

Carbinol Base (XI) *and Dye* (*oxalate*) (XII).—From the above leuco-base, the carbinol was prepared as described in the analogous cases above, m.p. 128-30° (decomp.), yield 75%.

The dye (oxalate) was prepared from the carbinol (XI) by the action of oxalic acid and ammonium oxalate. Crystallisation from dilute alcohol furnished a deep green powder, which decomposed with swelling above 175°, yield 75%. (Found : S, 10.52. $C_{54}H_{44}O_4N_8S_4$. $3C_2H_2O_4$ requires S, 10.11 per cent).

Di-(4-p-*ethoxyphenyl*-2-*aminothiazyl*-5-)-*phenylmethene* (XIII) was prepared from 4-*p*-ethoxyphenyl-2-aminothiazole (4.2 g.), benzaldehyde (0.93 g.) and HCl (conc., 12 c.c.) as described in previous cases and crystallised as a fine light yellow powder, m.p. 210° (decomp.), yield 90%. (Found : S, 12.17. $C_{29}H_{28}O_2N_4S_2$ requires S, 12.12 per cent).

Carbinol Base (XIV) *and Dye* (*oxalate*) (XV).—The carbinol base was prepared from the leuco-base by oxidation with lead dioxide ; when the oxidation was complete, the colour of the solution was deep green. After basification the colour changed to deep rosy. Crystallisation from alcohol yielded a deep brown compound, m.p. 130°, yield 85%.

The dye was prepared as described in the analogous cases above and it appeared as a blue-green powder, m.p. 195°, yield 60%. (Found : S, 9.90. $C_{58}H_{52}O_4N_8S_4$. $3C_2H_2O_4$ requires S, 9.98 per cent).

Grateful thanks of the author are due to Dr. M. K. Rout, Ph.D., Reader in Chemistry, Ravenshaw College, Cuttack, for suggesting the problem and for his guidance.

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Received November 9, 1955

[Jour. Indian Chem. Soc , Vol. 33, No. 6, 1956]

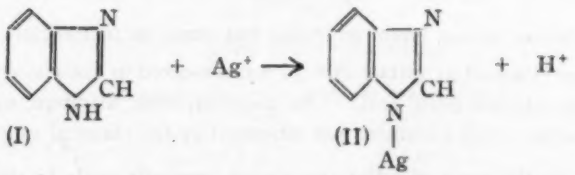
BENZIMIDAZOLE AS A REAGENT FOR SILVER *

By R. L. Dutta

Benzimidazole has been found to precipitate silver quantitatively in ammoniacal medium. In presence of ammoniacal ethylenediamine tetra-acetate, benzimidazole precipitates only silver, whereas copper, nickel, cobalt, iron, manganese, chromium, cadmium, zinc, mercury, magnesium, etc. remain in solution. Beryllium, titanium, aluminium, uranyl, thorium etc. have been masked by tartrate ion. But in presence of ammonium salts, precipitation is incomplete In the absence of ammonium salts therefore benzimidazole serves as a specific reagent for silver. The silver benzimidazole precipitate is stable towards heat and light, and a single determination takes much less time as compared to the classical chloride method.

Benzimidazole (I) $C_7H_6N_2$ has long been shown by Feigl and Gleich (*Monatsh.*, 1928, **49**, 385) to furnish well-defined salts with copper, cobalt, zinc, cadmium and mercury. The reaction between cobalt and benzimidazole has been used as a test for cobalt (Yagoda, *Michrochem.*, 1938, **24**, 117). Ghosh (this *Journal*, 1951, **28**, 710) has described the preparation of some more copper and nickel complexes and made their magnetic measurements. Recently Ghosh and Ghosh (*Proc. Ind. Sci. Congress*, 1955, Part III, p. 79) have reported gravimetric estimation of cobalt with this reagent at p_H 10. Although rather similar benzotriazole and its 5-bromo derivative have been used by various workers (Remington and Moyer, Dissertation, Abst. No. 24, Ohio State Univ. Press, 1937 ; Tarasevich, Vestnik Moskow Univ., 1948, **3**, No. 10, 161 ; Cheng, *Anal. Chem.*, 1954, **26**, 1038) as a reagent for gravimetric estimation of silver, so far no work with benzimidazole as a reagent for the same element has been reported.

It has now been found that benzimidazole furnishes with silver in ammoniacal medium a white quantitative precipitate (II), which is very stable towards light and heat.



(I) (II)

In presence of ammonia, the precipitate coagulates very rapidly and offers no difficulty in filtration. The precipitate is insoluble in hot water, dilute ammonia and benzene, but soluble in acids, pyridine, sodium thiosulphate and potassium cyanide. The composition of the precipitate, when dried at 120°, is $AgC_7H_5N_2$, so that the gravimetric factor for silver becomes 0.4797.

* After this paper was communicated, Ghosh and Ghosh (*Proc. Ind. Sci. Congress*, 1956, Part III, p. 58) have reported the use of benzimidazole for gravimetric estimation of silver in presence of thallium. But di-sodium salt of EDTA or sodium potassium tartrate has not been used for masking other interfering ions.

In presence of ammonia, besides copper, nickel, cobalt, zinc, mercury and cadmium, which give characteristic precipitates with benzimidazole, many other metals, hydroxides of which are insoluble in ammonia, interfere. However, it has been found that if ammoniacal ethylenediamine tetra-acetate (EDTA) is present, benzimidazole precipitates only silver, whereas many other metals are held in solution. Thus Cu, Ni, Co, Mn, Fe, Cr, Mg, Tl^{I}, Hg^{II}, Pb, Zn, Cd, etc. have been rendered harmless. Hydroxides of metals like titanium, beryllium are insoluble in EDTA ; so they have been masked by tartrate ion. Aluminium, thorium, uranyl also have been masked by tartrate ion. Hg^{I} will not interfere when oxidised to Hg^{II} state. Similarly, Fe^{II} must be oxidised to the Fe^{III} state becacuse Fe^{II}-EDTA reduces Ag^{+} to the metallic state (Pribil *et al.*, *Chem. Listy*, 1953, **47**, 88). But the most objectionable interference has been presented by ammonium salts. In presence of ammonium salts, precipitation of silver benzimidazole is incomplete, and consequently the values are low. It may be pointed out here that none of the workers on benzotriazole (*loc. cit.*) has studied the influence of ammonium salts. The present author intends to investigate this point in near future. Of the anions, nitrate, sulphate, acetate, chloride, phosphate, tungstate, vanadate, oxalate, chromate, etc. do not interfere. Thus, in the absence of appreciable quantity of ammonium salts, benzimidazole has been found to be a specific reagent for silver.

Experimental

o-Phenylenediamine (13.5 g.) was heated with 85% formic acid (8.5 c.c.) on a water-bath for about 2 hours. The mixture after cooling was treated with 10% NaOH till distinctly alkaline. The separated benzimidazole was filtered off and finally recrystallised from hot water (yield 10 g.), m. p. 169° (lit. m.p. 170°).

As the reagent was poorly soluble in cold water, a hot 1% aqueous solution was used as the precipitant.

Ammoniacal EDTA solution : Disodium salt of EDTA (7.5-11 g.) was dissolved in 100 c.c. solution containing 20 c.c. liquor ammonia and then filtered.

Ammonia solution : 20 c.c. liquor ammonia was made up to 100 c.c.

Silver solution : Pure silver nitrate (6.8 g.) was dissolved in 400 c.c. water containing a few drops of concentrated nitric acid. The solution, after filtration, was stored in an amber-coloured bottle. Silver content was estimated by the classical chloride method.

All solutions for the study of interference were generally made by direct weighing.

All reagents used in this investigation were either of Merck's G. R. or Extra pure variety or B.D.H. Analar quality. The EDTA, however, was a B.D.H.-L.R. grade. All p_H adjustments were made with a Cambridge p_H-meter.

Effect of p_H on the Precipitation of Silver.—It was observed that precipitation in slightly acid medium afforded a colloidal, incomplete product, which took a long time (2 hrs.) on the water-bath for coagulation. On the other hand, in ammoniacal medium the precipitates coagulated within 10 to 15 minutes, and good results were obtained.

TABLE I

Silver taken = 0.1080 g.

...	...	5.64	6.14	7.54	8.40	9.06	10.02
Silver found (in g.)	...	0.1053	0.1073	0.1077	0.1075	0.1076	0.1076

Procedure.—To the silver solution (in a volume of 50 c.c.) 10 c. c. of the ammonia solution was added to bring the p_H to the vicinity of 10. The solution was then heated on a water-bath to 60°-70° for about 10 minutes. It was then treated with an excess of a hot 1% reagent solution with constant stirring. Generally, for 100 mg. silver, 20 c.c. of the hot reagent solution was sufficient for complete precipitation. The mixture was then digested on the water-bath for another 10 minutes by which time the precipitate coagulated completely. The precipitate was then filtered through a Gooch crucible (G_3 or G_4) and washed with about 100 c.c. of warm water. The precipitate was finally dried at 120° to a constant weight (about 1½-2 hours) and weighed as $AgC_7H_5N_2$. Good results were obtained with silver content varying from 10 mg. to 100 mg. For amounts below 5 mg., a micro adaptation of the method is, however, preferable.

TABLE II

Silver taken.	Silver benzimidazole.	Silver found.	Error.
0.1104 g.	0.2318 g.	0.1112 g.	+0.0008 g.
0.0324	0.0676	0.0324	±0
0.0108	0.0224	0.01074	−0.00006
0.0054	0.0112	0.00537	−0.00003

Effect of Ammonium Salts.—It was observed that in presence of an appreciable amount of ammonium salts, precipitation of silver benzimidazole was incomplete ; consequently the values were low. So if the silver solution is strongly acidic, neutralisation must be made with dilute NaOH.

TABLE III

Silver taken = 0.1104 g.

Ammonium salt.	Amount added.	Silver benzimidazole.	Silver found.
NH_4NO_3	0.5 g.	0.2315 g.	0.1110 g.
	1.0	0.2288	0.1097
NH_4Cl	5.0	0.2183	0.1047
	1.0	0.2117	0.1016

Procedure in presence of Cu, Ni, Co, Mn, Mg, Hg^{II}, Pb, Zn, Cd, Tl, *etc.*—To the silver solution containing any of these interfering metals was added with stirring 10 c.c. of the ammoniacal EDTA solution and the mixture was then brought to 60°-70° and silver precipitated by excess benzimidazole. Generally, 2 to 3 times the theoretical amount of EDTA, required to complex a particular metal, was used to hold the metal in solution. For metals like iron and chromium, hydroxides of which were slowly acted upon by EDTA, this procedure had to be modified.

Procedure in presence of Iron and Chromium.—To the slightly acid solution of silver and these metals was added 10 c.c. of the simple EDTA (without ammonia), and the mixture was heated at 60°-70° for 5-10 minutes, when the metals were firmly complexed. A little precipitate of Ag-EDTA appeared which, however, dissolved on proper stirring when the solution was made ammoniacal by the addition of 10 c.c. of ammonia solution. Before the addition of the reagent, it was made sure that no silver-EDTA precipitate remained undissolved.

Procedure in presence of Al, Be, Ti, UO_2, Th, *etc.*—Aluminium, beryllium, titanium, etc. were masked by sodium potassium tartrate. To the slightly acidic solution of silver and these metals was added enough (5-10 g.) Rochelle salt (R.S.) and the mixture was afterwards made ammoniacal with 10 c.c. of ammonia solution. If a precipitate of the hydroxide forms, then some more tartrate should be added and the mass nearly boiled to get a clear solution. Afterwards, silver is precipitated as usual with the hot 1% reagent.

TABLE IV

ons added.	Amount added.	Ag. found.	Ag. taken.	Ions added.	Amount added.	Ag found.	Ag taken.
Cu^{2+}	63.5 mg.	0.1096 g.	0.1104 g.	Mg^{2+}	24.3 mg.	0.1094 g.	0.1104 g.
,,	,,	0.0539	0.0540	,,	,,	0.0547	0.0552
Ni^{2+}	58.7	0.1077	0.1080	Mn^{2+}	54.9	0.0536	0.0540
,,	,,	0.0545	0.0540	Al^{3+}	54	0.1112	0.1104
Pb^{2+}	207.2	0.1074	0.1080	,,	,,	0.0553	0.0552
,,	,,	0.0537	0.0540	Be^{2+}	18	0.1110	0.1104
Zn^{2+}	65.3	0.1084	0.1080	,,	,,	0.0553	0.0552
,,	,,	0.0539	0.0540	Ti^{3+}	47.9	0.0555	0.0552
Co^{2+}	59.0	0.1094	0.1104	,,	,,	0.1103	0.1104
,,	,,	0.1065	0.1080	UO_2^{2+}	270	0.1103	0.1104
Cd^{2+}	112.4	0.1070	0.1080	,,	,,	0.0556	0.0552
,,	,,	0.0539	0.0540	Th^{4+}	232	0.0556	0.0552
Hg^{2+}	200	0.1070	0.1080	,,	,,	0.1106	0.1104
,,	,,	0.0536	0.0540	WO_4^{2-}	248	0.1108	0.1104
Tl^{+}	204	0.1078	0.1080	,,	,,	0.0556	0.0552
,,	,,	0.0542	0.0540	VO_4^{3-}	57	0.1106	0.1104
Fe^{3+}	55.8	0.0532	0.0540	,,	,,	0.0553	0.0552
,,	,,	0.1070	0.1080	CrO_4^{2-}	116	0.1103	0.1104
I^{-}	52.1	0.1110	0.1104	,,	,,	0.0552	0.0552
,,	,,	0.0552	0.0552	$C_2O_4^{2-}$	88	0.1093	0.1104
				,,	,,	0.0546	0.0552
				HPO_4^{2-}	95	0.0547	0.0552

Composition of the Precipitate.—The silver benzimidazole precipitate was dried at 120° and then a weighed amount was decomposed by dilute nitric acid ; silver was then determined as chloride. (Found : Ag, 48.3. $AgC_7H_5N_2$ requires Ag, 47.97 per cent).

Author's grateful thanks are due to Prof. P. Rây and to Dr. P. C. Banerjee for their encouragement and good wishes during the course of this investigation. Thanks are also due to the Ministry of Education, Government of India, for the award of a Senior Research Scholarship which enabled the author to undertake this investigation.

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Received October 11, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 6, 1956]

ANALYTICAL ASPECTS OF SOME ORGANIC COMPOUNDS. PART IV. DETERMINATION OF THORIUM WITH 1-HYDROXY-2-NAPHTHOIC ACIDS

By Sachindra Kumar Datta

Thorium has been estimated by 1-hydroxy-, 1-hydroxy-4-bromo- and 1-hydroxy-4-nitro-2-naphthoic acids at p_H ranges from 3 to 5.2. Thorium may be separated from cerite earths and monazite sand. The common metals like Ba, Ca, Sr, Mg, Zn, Ti, etc. do not interfere. Thorium could not be separated from zirconium with these acids.

In the previous part (Datta, this *Journal*, 1956, **33**, 257) it was shown that 1-hydroxy-2-naphthoic acid and its bromo and nitro derivatives could be used for the quantitative determination of zirconium. These acids also afford a quantitative precipitation of thorium. Its estimation and separation from cerite earths and other metals have been described in the present paper. It is seen that of the three acids used, 1-hydroxy-4-bromo-2-naphthoic acid is the most effective precipitating agent for thorium ; it produces quantitative precipitation at p_H range of 3.6 to 5.2, while the corresponding p_H^* ranges for the 1-hydroxy-2-naphthoic acid and its nitro compound are 4.2 to 5.2 and 3.9 to 5.2 respectively. The sodium salt of the free acid may be more conveniently used than the free acid. Thorium may be separated from the cerite earths and from most of the common elements, excepting zirconium, which is precipitated almost within the same p_H range as thorium. Thorium may also be extracted from monazite sand with these reagents.

Experimental

The 1-hydroxy-2-naphthoic acids were prepared and purified according to the methods described previously (Datta, *loc. cit.*). A stock solution of thorium nitrate (Merck's reagent quality) was prepared and its thorium content was determined by the standard oxalate method. The stock solutions of other metals were prepared either from their chlorides or nitrates (all reagent grades) and their metal contents determined by standard methods.

Procedure.—To an aliquot amount of thorium solution, made neutral to Congo red and heated below its boiling temperature, was added a hot 0.5% solution of 1-hydroxy-2-naphthoic acid. In the case of its sodium salt and the bromo and the nitro compounds, 1% solution in water (hot) was used. No precipitation appeared immediately, but on adding about 1 c.c. of 2% ammonium acetate solution, precipitate came down in all cases. The solution was further heated over the free flame for 2 minutes, but was not boiled, so that the precipitate became coarser and settled at the bottom of the beaker. The colour of the precipitates with 1-hydroxy-2-naphthoic acid and its bromo and nitro compounds was white, orange and yellow respectively. The precipitates were filtered, washed with hot water several times and

then dried at 100° and ignited to the oxide to a constant weight. The results have been tabulated below. It is evident from Table I that up to 0.0071 g. of thorium may be estimated from 50 c.c. solution by the sodium salt of 1-hydroxy-2-naphthoic acid, but with bromo and nitro compounds, up to 0.0036 g. of thorium may be determined with nearest accuracy.

TABLE I

Estimation of thorium with 1-hydroxy-2-naphthoic acids.

Thorium soln. = 50 c.c.

[-N indicates -2-naphthoic acid]

No.	ThO_2 taken.	ThO_2 found by			
		1-OH-N.	1-OH-N. (Na-salt)	1-OH-4-Br-N.	1-OH-4-NO_2-N.
1.	0.0426 g.	0.0423 g.	0.0424 g.	0.0426 g.	0.0426 g.
2.	0.0284	0.0281	0.0282	0.0283	0.0282
3.	0.0036	0.0024	0.0026	0.0032	0.0031
4.	0.0018	...	...	0.0013	0.0017

Influence of p_H on the Precipitation of Thorium.—Buffer solutions in the p_H range of 2 to 6 were prepared according to standard directions. The procedure was to place 25 c.c. of the thorium nitrate solution, 50 c.c. of the buffer solution and 25 c.c. of the reagent solution in a 250 c.c. beaker and to heat the mixture below its boiling temperature with the subsequent addition of 1 c.c. of 2% ammonium acetate solution. The resulting precipitate was converted into the oxide in the usual manner. In all cases, a three to four fold excess of the reagent was added. The results are shown in Table II.

TABLE II

ThO_2 taken = 0.0178 g.

Reagents.	ThO_2 found at p_H			
	3.9	4.2.	4.7.	5.2.
1-OH-N	0.0172 g.	0.0173 g.	0.0174 g.	0.0174 g.
1-OH-N (Na-salt)	0.0173	0.0175	0.0176	0.0176
1-OH-4-Br-N	0.0176	0.0178	0.0178	0.0177
1-OH-4-NO_2-N	0.0174	0.0176	0.0177	0.0177

Separation of Thorium from the Cerite Earths.—Different amounts of standard cerium nitrate or lanthanum nitrate solutions were added to a definite quantity of thorium solution. The mixture was neutralised to Congo red and thorium was precipitated by all the reagents, as described before, and estimated as oxide. The results indicated in Table III show that thorium may be separated, with slight contamination, from solutions having thoria-earth oxide ratio up to 1:10 with the sodium salt of 1-hydroxy-2-naphthoic acid by single precipitation method, the corresponding ratios for bromo and nitro compounds are 1:16 and 1:14 respectively. The slight contamination, however, may easily be removed by double precipitation.

TABLE III

ThO_2 taken = 0.0142 g.

CeO_2 added.	La_2O_3 added.	Thoria : *RO.	ThO_2 found.	CeO_2 added.	La_2O_3 added.	Thoria : *RO.	ThO_2 found.	CeO_2 added.	La_2O_3 added.	Thoria : *RO.	ThO_2 found.
With 1-OH-N (Na-salt).				With 1-OH-4-Br-N.				With 1-OH-4 NO_2-N.			
0.0276 g.	...	1 : 2	0.0143 g.	0.0552 g.	0.0304 g	1 : 6	0.0144 g.	0.1104 g.	0.0304 g.	1 : 10	0.0145 g.
0.0276	0.0152 g.	1 : 3	0.0145	0.1104	0.0608	1 : 12	0.0145	0.1104	0.0912	1 : 14	0.0148
0.0552	0.0304	1 : 6	0.0146	0.1104	0.0912	1 : 14	0.0147	0.1104	0.1012	1 : 15	0.0151
0.0114	0.0304	1 : 10	0.0148	0.1104	0.1216	1 : 16	0.0148				

* RO stands for earth oxide.

Separation of Thorium from other metals.—Measured amounts of thorium nitrate solutions were added to definite quantities of metal salt solutions. The mixtures were brought to suitable p_H values by buffer solutions and the precipitation of thorium was carried out with these reagents as before. The precipitates were filtered, washed and ignited as usual. It is seen that Ca, Ba, Sr, Zn, Mg, Al, Cr, Mn and Ti do not cause any interference or coprecipitation. Metals like iron, cobalt and nickel are found to contaminate, though very slightly, the thorium precipitate; so double precipitation in those cases is necessary. Thorium cannot be separated from zirconium by these acids, as the latter is quantitatively precipitated almost within the same p_H range as the former. The results are recorded in Table IV.

TABLE IV

ThO_2 taken.	Metal oxide added.		ThO_2 found by Na salt of 1-OH-N.	ThO_2 found by 1-OH-4-Br-N.	ThO_2 found by 1-OH 4-NO_2-N.
0.0142 g.	BaO,	0.0250 g.	0.0142 g.	0.0143 g.	0.0143 g.
,,	SrO,	0.0218	0.0140	0.0143	0.0142
,,	CaO,	0.0316	0.0140	0.0144	0.0142
,,	Al_2O_3	0.0232	0.0143	0.0143	0.0144
,,	*Fe_2O_3,	0.0181	0.0144	0.0144	0.0143
0.0284	Cr_2O_3,	0.0232	0.0285	0.0286	0.0285
,,	MnO_2,	0.0105	0.0281	0.0282	0.0284
,,	ZnO,	0.0153	0.0281	0.0282	0.0283
,,	MgO,	0.0150	0.0282	0.0284	0.0285
,,	TiO_2,	0.0252	0.0280	0.0282	0.0283
,,	* CoO,	0.0167	0.0287	0.0286	0.0287
,,	* NiO,	0.0266	0.0286	0.0285	0.0287

* Indicates double precipitation.

Separation of Thorium from Uranium.—Thorium may also be separated from uranium to a great extent. Uranium is not precipitated with these reagents but a

slight quantity is held up by the thorium precipitate, when the latter is precipitated from mixtures having larger amounts of uranium. The separation limit for uranium has been determined, as uranium is found to occur along with thorium in nature. Thorium was therefore precipitated with these reagents from mixtures having different proportions of thorium and uranium by following the same procedure. The sodium salt of 1-hydroxy-2-naphthoic acid may separate thorium from solutions having thoria-uranium oxide ratio up to 1:6 by double precipitation method ; the corresponding ratios for the bromo and nitro compounds are 1:15 and 1:20 respectively. The results are recorded in Table V.

TABLE V

ThO_2 taken	U_3O_8 added.	$ThO_2 : U_3O_8$.	1 OH-N (Na-salt).	ThO_2 found by 1-OH-4-Br-N.	1-OH-4-NO_2-N.
0.0104 g.	0.0424 g.	1:4	0.0106 g.	0.0103 g.	0.0103 g.
,,	0 0636	1:5	0 0106	0.0104	0 0106
,,	0.1060	1:10	0.0112	0.0105	0.0106
0.0142	0.1696	1:12	...	0.0145	0.0146
,,	0 2120	1:15	...	0.0147	0.0148
,,	0 2756	1:19	...	0.0147	0.0150
,,	0.2862	1:20	...	0.0148	...
,,	0.3604	1:25	...	0.0151	...

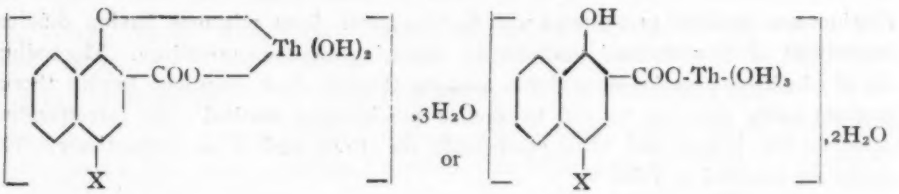
Extraction of Thorium from Monazite Sand.—Acid extract of a sample of Travancore monazite sand was prepared according to the method of Raghava Rao *et al.* (this *Journal*, 1950, **27**, 458). Thorium was estimated in this extract by single precipitation as before. Estimation with *m*-nitrobenzoic acid was also carried out side by side to compare the results, which are shown in Table VI.

TABLE VI

Wt. of Monazite.	ThO_2 obtained With Na-salt of 1-OH-N.		ThO_2 obtained With 1-OH-4-Br-N.	
1. 1.3250 g.	0.0969 g.	7.32%	0.0970 g.	7.32%
2. 1.5031	0.1098	7.31	0.1120	7.32
3. 1.1232	0.0822	7 32	0.0821	7.31
	With 1-OH-4-NO_2-N.		With *m*-nitrobenzoic acid.	
1. 1.3250	0.0968	7.31	0.0967	7 30
2. 1.5031	0 1098	7.31	0.1097	7.30
3. 1.1232	0 0822	7.32	0.0821	7.31

Composition of Thorium Salt of 1-Hydroxy-2-naphthoic Acid.—Thorium salts of these acids were prepared as usual. The salts were washed with hot alcohol several times in order to remove the free reagents, if any, and then washed with ether and dried at 120°-125°. Aliquot quanities were ignited to the oxide in a platinum crucible

and weighed to a constant weight. The results obtained suggest the following formula for the thorium salts of these acids.



The latter formula seems to be more probable for thorium ; direct weighing method for the estimation of thorium, however, is not practicable.

The author wishes to express his gratitude to Dr. S. S. Guha Sircar for his kind advice and suggestions. His thanks are also due to Prof. D.N. Dasgupta for his kind encouragement and providing laboratory facilities.

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Received July 13, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 6, 1956]

THE VARIATION OF CATIONIC ACTIVITY IN COLLOIDAL CLAYS WITH CONCENTRATION OF THE DISPERSE PHASE

By A. Chatterjee

The variations of the activity of Na^+, K^+ and Ca^{2+} ions of clays, saturated with these ions, have been determined at various concentrations of the clays by means of clay-membrane electrodes. The ionic activities increase almost linearly up to a certain concentration of the clay (11%, 10% and 5% for Na-, K- and Ca- clays respectively) but afterwards the rate of increase slows down. The percentage dissociation of Na- and K- clays decreases sharply at first, followed by an increase, and a more or less flattened maximum at about 10-11%. Ca- clay, however, shows no initial decrease in dissociation which rises to a fairly sharp maximum at about 1.2% clay concentration.

The clay-membrane electrodes for the determination of cationic activities were developed by Marshall ("Colloid Chemistry of Silicate Minerals", Academic Press, 1949). Later on Marshall *et al.* (*loc. cit.*) and Marshall and Chatterjee (*J. Phys. Coll. Chem.*, 1950, **54**, 671) used the membrane electrodes to study the variation of metal-ion activities in course of neutralisation of acid colloidal clays with hydroxides and oxides of Na, K, NH_4, Ca, Mg and Ba. Mitra (D. Phil. Thesis, Calcutta University, 1954) using a number of Indian clays prepared clay-membrane electrodes suitable for measurement of ionic activities over a wide range, and reported measurement of Na^+, K^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+} ion activities with the help of the membrane electrodes. Cationic activity measurements, reported above, generally refer to dilute suspensions, and the results are often applied directly to investigate ion-exchange characteristics of clay, present in soil. The clay, present in soil, is more or less gel-like and hardly assumes a sol state under the natural conditions. Hence, there may be little justification in extrapolating information available in dilute solutions to concentrated pastes.

The present enquiry aims at an understanding of the variation, if any, of Na^+, K^+ and Ca^{2+} ion activities of clays with the concentrations of the latter.

Experimental

The clay-membrane electrodes used in this investigation were prepared according to the method of Mitra (*loc. cit.*) by the usual process of evaporating clay suspensions into thin films and heating them to desired temperatures. The standardisation and performance of clay membranes as electrodes were thoroughly studied in this laboratory (Mitra, *loc. cit.*). The clay membranes, fixed to one end of a pyrex tubing, separated the base-saturated clay suspension or paste and a solution of known ionic activity (of say, NaCl, KCl or $CaCl_2$). The potential difference across the membrane between two tiny calomel electrodes was measured with the help of a Cambridge potentiometer. The ionic activity was calculated from E.M.F. of the following cell, according to the Nernst relation,

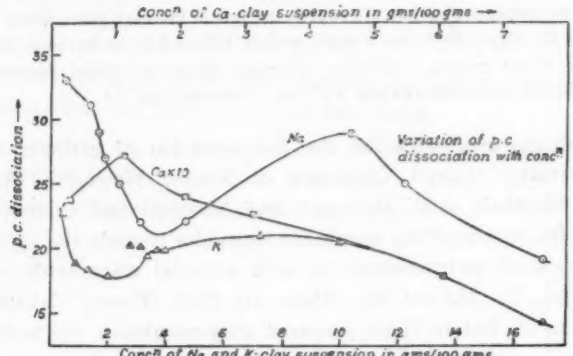
$$E = \frac{RT}{nF} \ln \frac{a\ (\text{solution})}{a\ (\text{clay})}$$

Hg, Hg_2Cl_2, Na (K/or Ca) Cl | Membrane | Na (K or Ca) clay, Hg_2Cl_2, Hg.

The variation of cationic activity with concentration of the clay was studied in the following manner. The clay was first concentrated by slow evaporation to a pasty mass. The solid content was determined by oven-drying a known weight of the paste. The diluted suspensions were then obtained from the pastes by adding known amounts of water, which was allowed to equilibriate for 96 hours.

The results of a_{Na}, a_K and a_{Ca} determinations are shown graphically in Figs. 1 and 2 and recorded in Tables I-III.

FIG. 1



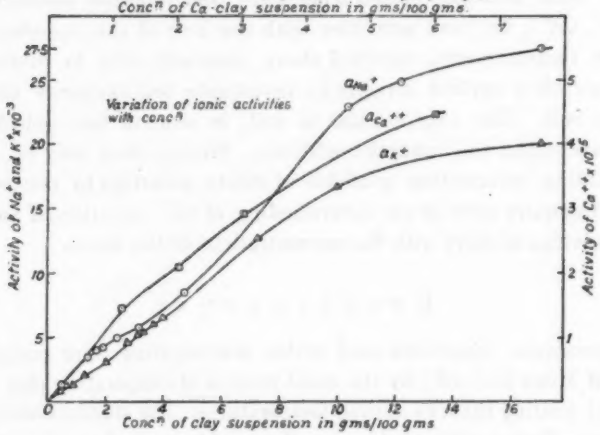

Conc^n of Ca-clay suspension in gms/100 gms
Variation of ionic activities with conc^n
a_{Na^+}
$a_{Ca^{++}}$
a_{K^+}
Activity of Na^+ and $K^+ \times 10^{-3}$
Activity of $Ca^{++} \times 10^{-5}$
Conc^n of clay suspension in gms/100 gms

FIG. 2

DISCUSSION

The nature of variation of activity of Na^+ and K^+ ions in the respective clays with the concentration of the latter is more or less the same. There are, however, two points of difference. Firstly, the initial slope is slightly higher for Na-clay, and secondly, the curve is much less steep after an almost linear relation up to 10% in the case of K-clay and little above 11% in the case of Na-clay. It is probable that the more hydrated Na^+ ion prevents, at least partially, overlapping of the double layer as the sol becomes concentrated so that the activity of Na^+ ions is not lowered to that extent which occurs in K-clay.

The effect of ion hydration becomes more evident in the Ca-clay, particularly when it is compared with Na- and K- clays. The initial slope equals that of Na-clay, but the rise in the activity of Ca^{2+} ion is prevented at a much lower (nearly 5%) concentration of the clay when as a result of relatively small hydration of Ca^{2+} ions, overlapping of the double layer is more likely.

Overlapping of the double layer is likely to result either in the increase in activity or in an 'immobilisation' of the ions. According to the latter process, those ions, which were registering their activity in dilute suspensions, become 'immobilised', so to say, with the result that the rate of increase in ionic activity due to the increase in concentration of the clay diminishes.

TABLE I

Known Na^+-ion activity = 0.0263.

No.	Clay/suspension (g./100 g.).	Total molal Na^+ conc. in clay (c).	E. M. F.	Na^+-activity of clay (a).	%Dissociation ($a/c \times 100$).
1	16.078	0.1401	−10 mV	0.02735	19
2	11.944	0.0985	1.6	0.02472	25
3	10.389	0.0857	3.4	0.02291	29
4	4.725	0.0389	28.9	0.00851	22
5	3.174	0.0262	38.5	0.00575	22
6	2.389	0.0197	42.4	0.00501	25
7	1.889	0.0156	47.4	0.00417	27
8	1.683	0.0139	48.0	0.00407	29
9	1.378	0.0114	51.4	0.00355	31
10	0.482	0.0040	74.9	0.00132	33

TABLE II

Known K^+-ion activity = 0.027.

No.	Clay/suspension (g./100 g.).	Total molal conc. of K^+ in clay (c).	E. M. F.	K^+ activity of clay (a).	%Dissociation ($a/c \times 100$).
1	16.960	0.1392	7.8 mV	0.01992	14
2	9.955	0.0821	12.4	0.01665	20
3	7.324	0.0604	19.4	0.01263	21
4	4.034	0.0333	35.8	0.00663	20
5	3.676	0.0303	28.4	0.00605	20
6	3.376	0.0278	41.3	0.00539	19
7	3.122	0.0257	42.7	0.00515	20
8	2.756	0.0227	45.6	0.00459	20
9	2.074	0.0171	56.1	0.00303	18
10	1.387	0.0114	65.6	0.00210	18
11	0.834	0.0070	77.9	0.00129	19
12	0.418	0.0035	95.5	0.00078	23

TABLE III

Known Ca^{2+}-ion activity = 0.0001.

No.	Clay/suspension (g./100 g.).	Total molal conc. of Ca^{2+} in clay (c).	E. M. F	Ca^{2+} activity of clay (a) × 10^5.	%Dissociation (a/c × 100).
1	6.088	0.0251	10.3 mV	4.48	0.18
2	3.143	0.0130	15.8	2.92	0.28
3	2.123	0.0088	20.0	2.10	0.24
4	1.289	0.0053	24.8	1.44	0.27
5	0.278	0.0012	46.1	0.27	0.24

Tables I, II and III record in the last column of each the percentage dissociation of the ion, calculated from the observed activity (a) and known concentration (c) of the ion present in the base-saturated clay. The percentage dissociation first decreases very sharply with concentration, but shows an increase at a higher concentration of the clay and continues to do so followed by a fairly sharp fall. The increase is shown by Na-clay at about 4-5%, and the same for K-clay is 2-3% ; the sharp fall almost coincides with the flattening of the activity curve. The graphs shown in figures represent the behaviour of Ca-clay which, unlike Na- and K-clay, shows no initial decrease of dissociation. On the other hand, the %dissociation reaches a maximum, followed by a sharp fall, as in the case of Na- and K-clays. The fall is observed at about 1.2% clay, whereas the concentration at which Ca^{2+} ion activity shows a decrease is higher.

Thanks of the author are due to Dr. S. K. Mukherjee of the University College of Science and Technology, for guidance, and to Prof. D. C. Ray, Vice-Principal, Vidyasagar College, for his kind interest.

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Received October 17, 1955

[Jour. Indian Chem. Soc., Vol. 33, No. 6, 1956]

STUDIES ON THE GELATION OF SILICIC ACID SOLS. PART IV. ON THE DEVELOPMENT OF YIELD VALUE AND STRUCTURE OF SILICIC ACID SOLS

By K. C. Sen and B. N. Ghosh

The rate of change of turbidity with time of silicic acid sols increases, becomes maximum approximately at or near the time of gelation and then gradually decreases. The time of gelation can be determined graphically from turbidity measurements. The viscosity of freshly prepared silicic acid sols is very low. As ageing continues it increases at first very slowly, then with appreciable speed and finally, a little before gelation, it shoots up to a very high value. A gradual increase in the extent of aggregation of silicic acid in the sol state is noticeable from the viscosity data of different systems by the application of Staundinger's viscosity relation Yield value develops roughly at about 75%, 80% and 86% of the time of gelation in the cases of sols prepared by using HCl, H_2SO_4 and H_3PO_4 respectively at room temperatures. Shaking prevents the formation of 'macro-structures' but does not hinder the formation of 'micro-structures' in silicic acid sols. Ultrafiltration of silicic acid sols in HCl system indicates that appreciable aggregation of silicic acid sols does not take place before 82% of the time of gelation at room temperatures.

The gelation of silicic acid accompanies changes in optical, viscous and polymerisation properties of the sol. Physical properties, such as turbidity and viscosity of the sol which are amenable to more accurate measurements, have been determined for the purpose of obtaining a more exact and reproducible value of the time of gelation. Since such measurements are easy to make, it has been possible to study the rate of gelation, starting from the freshly prepared sol, and thereby to gain an insight into the kinetics of the process. Furthermore, viscosity measurements enable calculation of the sizes of the particles. In this way it has been possible to get an idea of the state of aggregation of silicic acid molecules at various stages of gelation. Gelation is usually accompanied by the development of a certain kind of plasticity and the formation of structures. Viscosity measurements have also indicated at what stages of gelation plasticity develops. An attempt has also been made to ascertain whether physical factors like shaking have any effect on gelation. Ultrafiltration of a silicic acid sol has indicated the stage of gelation at which appreciable structure formation of silicic acid takes place.

Experimental

Turbidity

A freshly prepared silicic acid sol, irrespective of the acid used in its preparation, is transparent, almost like water, and the turbidity, Γ, is very low. With ageing turbidity

increased at first slowly, then with appreciable speed, then rapidly as the time of gelation was approached, after which it increased rather slowly and finally approached or tended to approach a limiting value. Some of these data are illustrated in Fig. 1. The turbidity of the sols was measured by Zeiss's Trubungsmesser in combination with a Pulfrich photometer. In the measurements done by the authors, red light and the same container for the sol were used throughout. The rate of change of tubidity, $\Delta\Gamma/\Delta t$, with time has been plotted against the corresponding time and the differential curves shown in Fig. 2 illustrate a few of them. It is found that in all the systems the time, t', corresponding to the maximum rate of increase in turbidity, is nearly equal to the time of gelation, t. The two from Fig. 2 are compared in Table I.

FIG 1

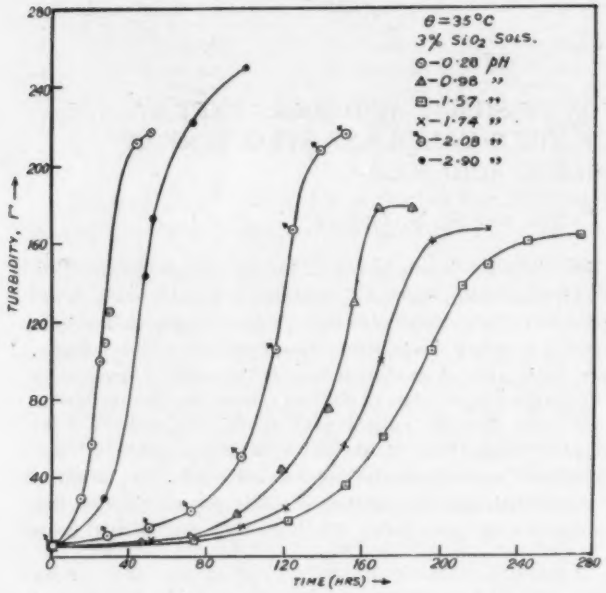


TABLE I

Temperature = 35°.

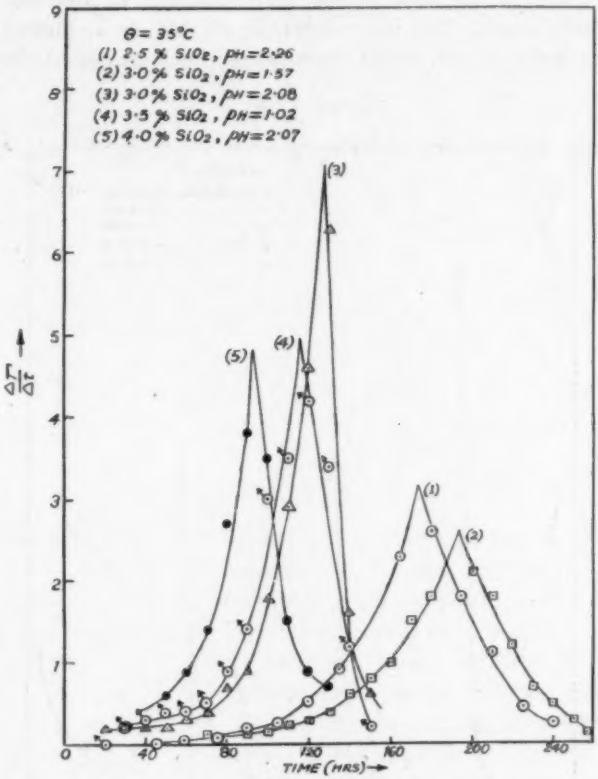
Curve No.	1	2	3	4	5
t' (hrs).	174	193	128	116	92
t (hrs.)	196	211	139	115	94

The time required for attaining the maximum rate of increase in turbidity may therefore be taken as a measure of the time of gelation, *i.e.*, the time of gelation of silicic acid sols can be determined graphically from tubidity measurements.

If the rate of change of turbidity is considered as a measure of the rate of gelation, the maximum rate of change of turbidity would correspond to the maximum rate of gelation. It suggests that the gelation process involves a chain mechanism, and the maximum rate of increase in turbidity corresponds to the completion of a definite fraction of the reaction. Theoretically therefore the maximum rate of increase in turbidity seems to

be a more accurate method of determining the time of gelation than the direct ones, e.g., the falling ball method.

FIG 2



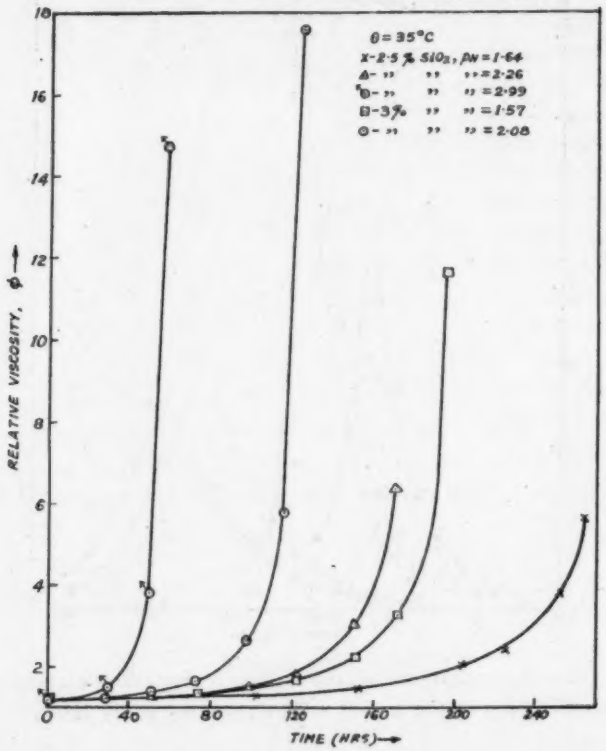
The limiting trubidity appears to be greater, the higher the temperature at which gelation occurs (studied only in the case of sols prepared by using HCl).

Viscosity

The relative viscosity of a large number of silicic acid sols was determined by the Ostwald viscometer at a constant temperature in the thermostat at different stages of ageing. Some of these data are illustrated in Fig. 3. The viscosity of the freshly prepared silicic acid sol was very low, irrespective of the acid used in its preparation. As ageing continued, it increased at first very slowly, then with appreciable speed and finally, a little while before gelation, it shot up to a very high value such that it became very difficult to take measurements with the viscometer. In the case of sols, prepared by using HCl or H_2SO_4, the initial viscosity was almost equal to that of water. It is possible in these cases to predict the approximate time of gelation from the viscosity-time curves. Thus, the relative viscocities, η, of sols obtained with HCl and H_2SO_4 attain values

equal to 2.0 and 3.0 at 55° at approximately 71% and 80% and at approximately 66% and 78% of the time of gelation respectively. The initial viscosities of sols obtained with other acids, although low, can vary within wide limits due to the presence of variable quantities of free acids, and so the approximate proportionality of viscosity to the time of gelation does not hold good. This is, however, applicable in a limited sense to the case of sols of a particular system, initial viscosities of which are almost identical.

FIG. 3



From the rate of change of viscosity with time it has been possible to visualise the degree of aggregation of silicic acid in the sol state by the application of Staundinger's viscosity relation,

$$\eta_{sp.} = \frac{\eta_1 - \eta_0}{\eta_0} = K.C.M. \quad \ldots \quad \ldots \quad (1)$$

where $\eta_{sp.}$ is the specific viscosity and η_0, the viscosity coefficient of the medium, K is a constant for the polymer, C is its concentration and M, the molecular weight.

The molecular weight of silicic acid in a number of sols at different stages of ageing has been calculated from equation (1) in terms of M_0, the assumed molecular weight in a freshly prepared sol. A gradual increase in the extent of aggregation of silicic acid

in the sol state is noticeable from the viscosity data of different systems. Results of two such sols in HCl system are illustrated in Table II.

TABLE II

Molecular weight (M) from specific viscosity.

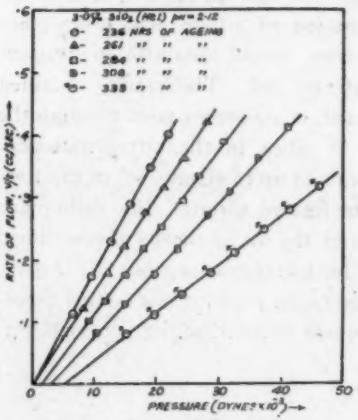
Temp. = 35°.

(*i*) SiO_2 conc. = 3.0%. p_H = 1.57.			(*ii*) SiO_2 conc. = 3.0%. p_H = 2.18.		
t.	$\eta_{sp.}$	*M.*	*t.*	$\eta_{sp.}$	*M.*
0 hr.	0.12	1.00 M_0	0 hr.	0.16	1.00 M_0
74	0.29	2.42	20	0.21	1.31
122	0.63	5.25	51	0.36	2.25
151	1.20	10.00	73	0.65	3.94
171	2.25	18.75	98	1.63	10.19
195	10.61	88.42	116	4.76	29.75
			124	16.58	103.60

Yield Value

The development of yield value by the silicic acid sols has been studied with the Bingham viscometer. Viscosity measurements of standard cane sugar solutions by this apparatus are found to be reproducible. If a freshly prepared silicic acid sol is forced through a capillary tube, the rate of flow is directly proportional to the applied pressure and the plot of the rate of the flow against the pressure gives a straight line passing through the origin. When plasticity develops, the plot of the flow against pressure, although a straight line, makes an intercept on the pressure axis, which is called the yield value. It has been found that the yield value develops roughly at about 75%, 80% and 86% of the time of gelation in the case of sols prepared by using hydrochloric, sulphuric and phosphoric acids at the room temperatures. The development of yield value in a particular sol, prepared with hydrochloric acid, is illustrated in Fig 4.

FIG. 4



Effect of Shaking

An attempt has also been made in the following way to gain information regarding the stage where structure formation preceding the gelation of silicic acid takes place. The

silicic acid sol, prepared with HCl, was divided into two parts. One was kept static, while the other was kept stirred continuously, except during measurements. The turbidity and viscosity (by Ostwald viscometer) of the two samples were determined at regular intervals. The turbidity of the sol in the shaker was always slightly greater than that of the sol at rest. It was also found that initially at any stage of ageing, the viscosities of the sol at rest were identical with those in the shaker. Sometime before gelation the viscosit of the sol in the shaker became slightly greater than that of the sol at rest. The sol in the shaker, however, never set to a gel ; when the sol at rest set to a gel the sample in the shaker was a very thick sol of high turbidity. If, however, a part of the thick sol in the shaker is allowed to remain at rest, gelation takes place within a few hours. This gel is generally weak and highly turbid.

The viscosity-time curves indicate that the viscosity of the sol in the shaker becomes slightly greater than that of the sol at rest at about 72% of the time of gelation. Comparing this observation with that noticed previously, it appears that the development of greater viscosity of the sol in the shaker roughly corresponds to the development of yield value of silicic acid sols. It is likely that shaking does not prevent the formation of micro-structures but perhaps hinders the development of macro-structures in silicic acid sols.

Ultrafiltration

Some information regarding the structure formation may possibly be obtained from a study of the ultrafiltrate of a silicic acid sol. A silicic acid sol (3.0% SiO_2), prepared with HCl, was allowed to age at the room temperature. A small fraction of the sol was filtered through cellophane paper at regular intervals and the silica concentration of the ultrafiltrate was determined. If structure formation of silicic acid takes place gradually the concentration of silica in the ultrafiltrate would diminish in a similar manner and becomes zero when the sol sets to a strong gel. The results obtained are recorded in Table III. The sol, when just prepared, completely passed through the cellophane. As ageing proceeded, the concentration of silica in the ultrafiltrate very slightly diminished and then remained practically constant up to about 82% of the time of gelation. A little before gelation the sol could not be filtered through the cellophane at all. An attempt to separate the dispersion medium of the sol by means of centrifugal forces, ten times as strong as the suction pressure used for ultrafiltration, failed. Again, when the sol had set to a strong gel but no syneresis had taken place, it was neither possible to filter nor to separate the dispersion medium by means of centrifuging (3200 r.p.m.).

TABLE III

3.0% SiO_2 sol (HCl). Time of gelation = 264 hours. p_H = 2.30.

Time (hrs.)	0	25	168	192	216	240	264	288	336
SiO_2 conc. in the ultrafiltrate	3.016	2.944	2.894	2.884	2.850	Could not be filtered.		1.064	0.889

Some time after gelation when syneresis took place, the gel could be separated from its dispersion medium with the help of a centrifuge. The complete separation was,

however, effected by ultrafiltration. The silica content of the ultrafiltrate was then determined. It is found that in this ultrafiltrate silicic acid is present only in relatively small amount.

Assuming that the difficulty in the ultrafiltration or in the separation of the dispersion medium is associated with the formation of macro-structures, it appears that the latter takes place in an appreciable extent not earlier than 82% of the time of gelation.

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Received December 23, 1953.

[Jour. Indian Chem. Soc., Vol. 33, No. 6, 1956]

STUDIES IN INDIGOID DYES. PART XVIII. THIOINDIGOID DYES DERIVED FROM FLUORENE-2-SULPHONIC ACID

By Paresh Chandra Dutta and Dasrath Mandal

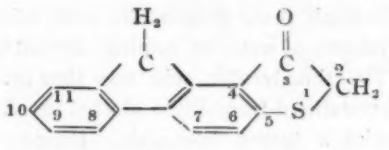
Hitherto-unknown 4 : 5-fluoreno-3-hydroxy-1-thiophene, prepared from fluorene 2-sulphonic acid, has been condensed with various *o*-diketones and the corresponding thioindigoid dyes have been obtained with a view to studying colour and its relation to chemical constitution.

Thioindigoid dyes derived from diphenyl-4-sulphonic acid were studied previously (Part XIII, this *Journal*, 1954, **31**, 827). In the present communication a study of similar dyes, derived from fluorene-2-sulphonic acid, has been made so that a comparison as regards the colour and dyeing properties between these two series of compounds could now be made. So far as the dyeing properties are concerned, it has been found that the dyes derived from diphenyl-4-sulphonic acid are superior in producing a deeper and fuller shade on cotton to those derived from fluorene-2-sulphonic acid, the latter, as a class, are found feebly soluble in alkaline hydrosulphite, and thus these produce a light shade. As regards the depth of colour, there is a slight difference, the fluoreno compounds appearing slightly deeper. A study of absorption spectra of these dyes will be the subject of a later communication when a definite conclusion could be arrived at.

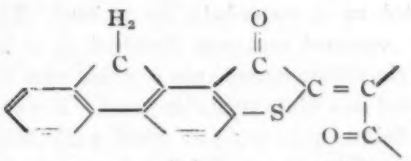
For the preparation of 4 : 5-fluoreno-3-hydroxy-1-thiophene, fluorene-2-sulphonic acid, prepared according to Hodgkinson and Mathews (*J. Chem. Soc.*, 1883, **43**, 166), was as usual converted successively into the sulphochloride, the mercaptan and the thioglycollic acid, all unknown, and this thioglycollic acid through its acid chloride was cyclised to the thioindoxyl. This thioindoxyl was then condensed with *o*-diketones for the preparation of these thioindigoid dyes. The *bis*-indigo was obtained as a bluish violet precipitate in small quantity by oxidising the indoxyl in alkaline solution with potassium ferricyanide. As the yield had been very small it was not further investigated. The crude, easily oxidisable thioindoxyl was dissolved in acetic acid and the acetic acid solution used for condensation with various *o*-diketones. The yield of the dyes has been fair in most of the cases. These dyes are insoluble in alcohol, slightly soluble in acetic acid and highly soluble in pyridine and nitrobenzene. In concentrated sulphuric acid they dissolve with a characteristic colour. They are not much soluble in alkaline hydrosulphite so that a light shade on cotton has generally been obtained.

The formation of a new five-membered ring due to the cyclisation of fluorene-2-thioglycollic acid may take place either in position-1 or 3 of the fluorene ring, but as in the formation of disubstitution products of fluorene from 2-substituted monocompounds the position-1 is attacked and 2 : 1-disubstitution products are obtained, it is presumed that in the formation of thioindoxyl in this case, position-1 has similarly been attacked and 4: 5-fluoreno-3-hydroxy-1-thiophene has been obtained.

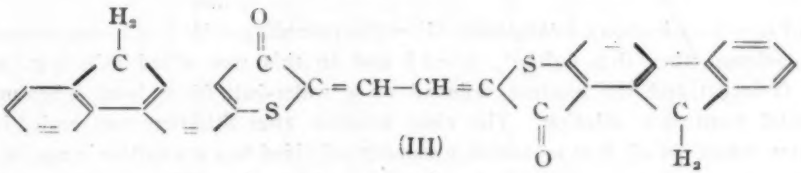
The structures of the indoxyl (I), the indigoid dyes (II), and the glyoxal compound (III) may therefore be represented as :



(I)



(II) Diketone



(III)

EXPERIMENTAL

Fluorene-2-sulphonic Acid.—Fluorene (16.6 g.) was dissolved in chloroform (75 c.c.) at room temperature and to this under ice-cooling a solution of chlorosulphonic acid (12 g.) in chloroform (30 c.c.) was added in small portions with vigorous shaking. The mixture became greenish and gradually the monosulphonic acid separated out as a dirty white precipitate. After allowing to stand for an hour at room temperature and frequent shaking, the mixture was filtered from chloroform and the residue boiled with water and filtered hot. The filtrate was then mixed with potassium carbonate till slightly alkaline, boiled and filtered. The filtrate on cooling separated white crystals of the potassium salt. It was recrystallised from hot water, yield 19 g.

Fluorene-2-sulphochloride.—Carefully dried and finely powdered potassium fluorene-2-sulphonate (50 g.) was mixed with PCl_5 (50 g.) and $POCl_3$ (20 c.c.) and heated in an oil-bath at 140° for an hour. $POCl_3$ was then distilled off under reduced pressure and the residue decomposed by ice and left overnight. The residue, after thoroughly washing with water and drying, was crystallised from chloroform, m.p. 159° (with previous shrinking at 155°) ; yield of crude sulphochloride, 40 g. (Found : C, 58.73 ; H, 3.52. $C_{13}H_9O_2ClS$ requires C, 58.98 ; H, 3.4 per cent).

Fluorene-2-thiol was prepared by reducing the sulphochloride with tin and HCl and heating the mixture for 10 hours. Some quantity of the thiol volatilised and collected as white shining flakes in the inner tube of the condenser. The residue, after cooling, was filtered, washed with HCl (conc.) and water, and extracted with benzene ; the benzene extract was dried by anhydrous calcium chloride, filtered and the benzene distilled off. The residue was then crystallised from alcohol as yellowish white flakes, m.p. 127°, yield 80-85%. (Found : C, 78.53 ; H, 5.18. $C_{13}H_{10}S$ requires C, 78.8 ; H, 5.05 per cent).

Fluorene-2-thioglycollic Acid.—The above thiol (10 g.) was dissolved in 10% caustic soda solution (50 c.c.) and to this after filtration was added a solution of monochloroacetic acid (5 g.), previously neutralised with caustic soda. The mixture was heated on a water-bath for an hour. The sodium salt of the thioglycollic acid, which had separated out, was dissolved in a large volume of water by heating, filtered hot and the filtrate immediately acidified with HCl. The thioglycollic acid was thus precipitated as a white crystalline mass. It was then crystallised from dilute alcohol as shining flakes, m.p. 143-44°, yield 9 g. While drying it turned brownish. (Found: C, 69.81 : H, 4.75. $C_{15}H_{11}O_2S$ requires C, 70.31 ; H, 4.68 per cent).

4 : 5-*Fluoreno*-3-*hydroxy*-1-*thiophene* (I).—The preceding acid (2 g.) was suspended in petroleum ether (b.p. 60°-80°, 20 c.c.) and to this was added PCl_5 (2 g.) and pyridine (2 drops), and the mixture refluxed on a water-bath for an hour, when most of the solid went into solution. The clear solution after filtration was cooled in a refregerator when an oil, first separated, gradually solidified to a crystalline mass, m.p. 85°. When prepared on a large scale, the oil could not be solidified. This solid or oil was redissolved in fresh petroleum ether (20 c.c.) and treated with anhydrous aluminium chloride (2 g.) and refluxed for 12 hours. The dark chocolate complex, after filtration, was decomposed by ice and HCl (conc.). The yellowish white substance, thus obtained, dissolves in dilute caustic soda on warming, forming a greenish solution and is precipitated by HCl as a curdy white solid, quickly becoming reddish due to oxidation. The yield is poor. The caustic soda solution with potassium ferricyanide produces a bluish violet precipitate of the *bis*-indigo with poor yield. For condensation with *o*-diketones, the acetic acid solution of the crude thioindoxyl has been used in all cases.

2-(4: 5-*Fluorenothiophene*)-3′-*indol-indigo* (IIa) was prepared by mixing an acetic acid solution of (I) with a solution of isatin in acetic acid and adding 5 drops of HCl (conc.). Immediately the solution became pink and a violet precipitate separated out. The mixture was heated for half an hour to ensure complete reaction and filtered hot, the residue washed with acetic acid and alcohol and crystallised from nitrobenzene as a violet crystalline mass, m.p. above 300°. It dissolves slightly in alkaline hydrosulphite with a yellow colour and dyes cotton in light pink shade. In H_2SO_4 (conc.) it dissolves with a violet colour. (Found: C, 74.9 ; H, 3.5. $C_{23}H_{13}O_2NS$ requires C, 75.2 ; H. 3.5 per cent).

2-(4 : 5-Fluorenothiophene)-3′-(6′-*bromo*)-*indol-indigo* (IIb), -3′-(5′ : 7′-*dinitro*)-*indol-indigo* (IIc), -2′-*acenaphthylene-indigo* (IId), -2′-(5′ or 6′-*bromo*)-*acenaphthylene-indigo* (IIe), -2′-(5′ or 6′-*nitro*)-*acenaphthylene-indigo* (IIf), -2′-(5′ : 6′-*dinitro*)-*acenaphthylene-indigo* (IIg), -9′-*phenanthrene-indigo* (IIh), -1′-*aceanthrylene-indigo* (IIi) were similarly prepared as compound (IIa) with the corresponding *o*-diketones (vide Table I). The dyes were crystallised from nitrobenzene. The m.p. of the compounds, crystalline shape, colour in H_2SO_4 (conc.), dyeing shade on cotton from hydrosulphite vat and mol. formula and analysis are recorded in Table I.

TABLE I

Dye No.	o-Diketone.	M. P.	Colour & crystal shape.	Colour in H_2SO_4.	Shade on cotton.	Formula.	Analysis Found.	Analysis Calc.
IIb	*m*-Bromoisatin	>300°	Dark violet mass	Light green	Light violet	$C_{23}H_{12}O_2NBrS$	C: 61.65% H: 2.87	61.88% 2.69
IIc	5:7-Dinitroisatin	Do	Greyish violet cryst. mass	Green	Chocolate violet	$C_{23}H_{11}O_6N_3S$	N: 8.9	9.19
IId	Acenaphthenequinone	Do*	Copper-red needles	Do	Violet	$C_{17}H_{14}O_2S$	C: 80.3 H: 3.6	80.6 3.48
IIe	5-Bromoacenaphthene-quinone	Do†	Violet needles	Do	Do	$C_{21}H_{13}O_2BrS$	C: 67.18 H: 2.9	67.36 2.7
IIf	5-Nitro- Do	Do	Dark mass	Light green	Light blue	$C_{27}H_{13}O_4NS$	C: 72.31 H: 3.2	72.48 2.97
IIg	5:6-Dinitro- Do	Do	Do	Violet	Green	$C_{27}H_{12}O_6N_2S$	N: 5.72	5.69
IIh	Phenanthrenequinone	Do	Do	Chocolate-violet	Light violet	$C_{29}H_{16}O_2S$	C: 80.93 H: 3.91	81.30 3.73
IIi	Aceanthraquinone	Do	Chocolate mass	Chocolate brown	Light brown	$C_{31}H_{16}O_2S$	C: 82.13 H: 3.65	82.3 3.54

* Shrinking at 290°.
† Subliming at high temp.

2-(4 : 5.*Fluorenothiophene*)-*elhylene-indigo* (III) was prepared by heating fluorenohydroxythiophene and glyoxal sodium bisulphite in acetic acid solution with the addition of 10 c.c. HCl (conc.), when gradually it separated out as a violet precipitate. It was obtained as a violet crystalline powder from nitrobenzene, m.p. above 300°. It dissolves in H_2SO_4 (conc.) with a violet colour and dyes cotton from brown hydrosulphite vat in light bluish violet shade. (Found : C, 81.43 ; H, 2.91. $C_{32}H_{16}O_2S_2$ requires C, 81.78 : H, 2.87 per cent).

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Received March 10, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 6, 1956]

ADSORPTION OF PHOSPHATE BY CLAY MINERALS
PART I. KAOLINITE AND HALLOYSITE

By P. R. Sinha

Adsorption of phosphate and other ions by kaolinite and halloysite, which are present in certain soil types, has been investigated. Adsorption of phosphate is appreciable, but of other ions, negligible. The results indicate that phosphate adsorption or anion exchange, in general, by kaolinite is rendered complicated by the presence of aluminium, either in the free state or present in the laterally broken down lattice of clay minerals when the latter are finely powdered. Removal of free alumina by means of dilute acid and/or treatment of phosphatised kaolinite with ammonium oxalate solution bring down the p.c a. to its normal low value. Analysis of the oxalate leachate shows the formation of definite aluminium phosphates on phosphatisation of kaolinite. This has been further confirmed with the help of electron diffraction pictures. The agreement between the p.a.c. and b.e c. of kaolinite has been explained by assuming that the surface OH groups act as the centre of both cation and anion exchange, depending on the experimental conditions. B.e.c. of halloysite has been found almost the same as of kaolinite, but p.a.c. is higher, particularly in acidic solution.

Soil being a heterogeneous body, the different types of constituents, which should be considered for a discussion on phosphate adsorption, are the silicate minerals, metallic oxides and organic matter. The last mentioned constituent does not play as much significant role in phosphate fixation as the others. There are two schools of thought on the subject. One regards it as a process of anion exchange and the other considers it as a chemical reaction. A review of the literature on phosphate fixation up to 1940 has been published by Midgley (*Soil Sci. Soc. Amer. Proc.*, 1940, **5**, 24). Some of the important papers published later were reviewed by the author in an earlier communication (Sinha and Chowdhury, this *Journal*, 1954, **31**, 211). Adsorption of tartrate by soil is very small, whereas citrate is not adsorbed at all, although both displace adsorbed phosphate. Dean and Rubins (*Soil Sci.*, 1947, **63**, 377) as well as Schollenberger (*ibid.*, 1947, **64**, 371) noticed that arsenate and phosphate were able to replace each other in the soil. Sieling (*Soil Sci. Soc. Amer. Proc.*, 1946, **11**, 161) noticed that neither phosphate nor arsenate was adsorbed by kaolinite which had been previously washed with acid to remove the free oxide, but adsorption took place when the sample was ground in a ball mill, and it was negligible when the ground sample was again washed with acid. He ascribed the adsorption of phosphate or arsenate to the formation of alumina as a result of grinding. Haseman *et al.* (*Soil Sci.*, 1950, **70**, 257) who studied the reaction at 90°, using a molar solution of phosphate, observed that kaolinite was almost completely decomposed and was converted into palmerite-like products.

Most of the studies on phosphate or anion adsorption were restricted to soil or its clay fraction, and this prevented a correct appraisal of phosphate adsorption. Amongst the studies with purer minerals, there are some with kaolinites, and a very few with montmorillonites. In this respect the work of Chatterjee and Datta (*J. Soil Sci.*, 1951, **2**, 224) covers a number of points. They studied the adsorption of phosphate

by H-kaolinite and H-montmorillonite under varying conditions of p_H, concentration of PO_4^{3-} and particle size. The part played by the free iron and aluminium oxides was particularly investigated and a correlation was observed between iron and alumina, brought into solution by dilute HCl at p_H 3.0, and PO_4^{3-} adsorbed at this p_H.

The present series of study has been conducted, keeping in view the heterogeneous nature of soil. Adsorption of phosphate by alumina was reported previously (Sinha and Chowdhury, *loc. cit.*). The work has also been extended to silicate minerals other than those usually present in soil. Thus, besides several kaolinites, montmorillonites and attapulgite, some micas, talc, pyrophillite and halloysite, etc. have been included in this study. Part I deals with the results obtained with kaolinite and halloysite.

Experimental

Kaolinite and Halloysite.—Two different samples, KaA and KaB, of kaolinite were used. The analytical as well as X-ray data of both the samples conform to those of the pure mineral. The entire clay fraction (consisting of particles $<2\mu$) of KaA was used, but in the case of KaB, particles having e.s.d. $2-0.5\mu$, which were fractionated by sedimentation, were employed. The samples were converted into their hydrogen forms. The analysis of kaolinite and halloysite* samples is shown in Table I.

Table I

	H_2O (110° to ignition).	SiO_2.	Al_2O_3.	Fe_2O_3.
KaA	13.85%	46.13%	39.62%	...
KaB	13.79	46.40	39.40	0.05%
Halloysite	17.90	43.92	38.35	...

Anion Adsorption.—The experimental procedure is the same as that used previously by Sinha and Chowdhury (*loc. cit.*, p. 213). For purposes of a comparative study the reaction, which went on very slowly after 4 or 5 days, was not usually prolonged beyond five days.

In some experiments, the adsorbed phosphate was leached out with solutions of ammonium nitrate, sulphate, oxalate, citrate or fluoride instead of NaOH or HNO_3. Before applying Pemberton's procedure for phosphorus determination, the phosphate was precipitated as ferric phosphate in the sulphate as well as in fluoride leachate after removal of fluoride; oxalate and citrate were decomposed by boiling with strong nitric acid.

Magnesium was determined either by the oxine method after separation of phosphate or according to Handy's method of titrating the $Mg(NH_4)PO_4$ with standard acid. In the absence of phosphate, Al was estimated by the oxine method.

For the determination of silica the oxalate, citrate, etc. were first decomposed by baking and ignition. Table II records the data on the adsorption of phosphate and other anions by KaA.

* Sample received from Prof. T. F. Bates, Pennsylvania (U.S.A.) to whom the author's thanks are due.

TABLE II

Adsorption of anions by KaA.

B.e.c. = 4·0 m.e.*

Solution.	Anion adsorbed (m.e./100 g.**).	Solution.	* Anion adsorbed (m.e./100 g.).
0.0125*N*-H_3PO_4	1.2	0.05*N*-K_2SO_4	Nil
0.02*N* ,,	2.0	0.05*N*-K_2SO_4 + H_2SO_4 (p_H 2·5)	,,
0.05*N* ,,	4.0	0.05*N*-K_2CrO_4	,,
0.066*N* ,,	6·5	0.05*N*-Oxalic acid	,,
N-$NH_4H_2PO_4$ (p_H 4.0)	8.0		

* By Parker's method (*J. Amer. Soc. Agron.*, 1929, **21**, 1030).

** Assuming that phosphorus is adsorbed as PO_4^{3-}.

The results demonstrate that even the clay fraction of kaolinite adsorbs only a small amount of phosphate and does not at all take up sulphate, chromate or oxalate.

DISCUSSION

Effect of Grinding of Kaolinite on Anion Adsorption.—Grinding has been found to increase anion adsorption, particularly phosphate. Stout (*Soil Sci. Soc. Amer. Proc.*, 1939, **4**, 177) suggested on the basis of X-ray and chemical analysis that OH groups released by grinding reacted with $H_2PO_4^-$ ions with the consequent loss of water. The characteristic X-ray diffraction of kaolinite was absent in phosphatised kaolinite but reappeared on removal of phosphate. Coleman (*Soil Sci.*, 1944, **58**, 71) attributed the major proportion of phosphate, adsorbed by kaolinitic and montmorillonitic clays and other fine clays, to the free aluminium oxide and ferric oxide present as impurities (cf. Chatterjee and Datta, *loc. cit.*).

The grinding of kaolinite, whether wet or dry (Shaw, *J. Phys. Chem.*, 1942, **46**, 1032) exposes a large number of OH groups, which along the lateral plane are composed of those lying between aluminium and silicon layers. Moreover, the breaking of Si-O-Al linkages leads in the presence of moisture to Al-OH groups. Aluminium oxide definitely possesses anion exchange and phosphate adsorption capacities. It is likely therefore that the OH groups attached to Al, which are exposed either by grinding or hydrolytic cleavage, are the centres of phosphate interaction. Ordinarily, kaolinite adsorbs a small amount of phosphate (Table II) but no sulphate or chromate. The basic function of the small number of Al-OH groups present is perhaps too weak to react with sulphate or chromate ions. Girnding increases the number of anion-exchange spots and as such, an increase of anion adsorption, more particularly of phosphate, is clearly noticeable (cf. Table III).

TABLE III

Adsorption of anions by ground kaolinite (KaA).

Solution.	p_H of soln.	Adsorbed anion (m.e./100g.).	Solution.	p_H of soln.	Adsorbed anion (m.e./100g.).	Solution.	p_H of soln.	Adsorb. anion (m.e./100g.).
0.0125*N*-H_3PO_4	2.52	102	0.05*N*-H_3PO_4 + K_2HPO_4	3.03	237	0.05*N*-Oxalic acid	1.75	8.7
0.025*N*- ,,	2.30	172	,, ,, ,,	3.6	250	0.05*N*-Na-oxalate	3.0	21.7
0.05*N*- ,,	2.05	237	,, ,, ,,	4.3	204	0.05*N*-K_2SO_4+H_2SO_4	2.52	11.6
0.0125*N*-K_2HPO_4	...	22	,, ,, ,,	6.4	105	0.005*N*-H_2SO_4	...	9.5
0.025*N*- ,,	...	25	,, ,, ,,	7.1	57	0.05*N*-Chromic acid	...	7.9
0.05*N*- ,,	...	32	,, ,, ,,	8.0	32	+K_2CrO_4	4.3	7.9
						0.05*N*-K_2CrO_4	9.0	Nil

Role of Aluminium in Anion-adsorption by Kaolinite.—A comparision of the above data with similar results obtained with Al_2O_3 sol (Table IV) clearly domonstrates the role of alumina in anion adsorption by kaolinite. Grinding as a method of increasing the surface of minerals has been variously questioned (Jackson and Truog, *Soil Sci. Soc. Amer. Proc.*, 1939, **4**, 136 ; Laws and Page, *Soil Sci.*, 1946, **62**, 319 ; Marshall, *J. Phys. Chem.*, 1937, **41**, 935 ; Perkins, *Soil Sci.*, 1948, **65**, 185 ; Sieling, *loc. cit.*). The formation of different aluminium phosphates in the reaction between ground kaolinite and phosphate solutions was shown by Ensminger (*Soil Sci. Soc. Amer. Proc.*, 1948, **13**, 170).

TABLE IV

Comparison of adsorption of anions by Al_2O_3 *sol and ground kaolinite.*

Solution	Absorption (m.e./100 g.) by Al_2O_3 sol.	Ground kaolinite.
0.05*N*-H_3PO_4	527	237
0.05*N*-KH_2PO_4	250	105
0.05*N*-K_2HPO_4	180	32
0.05*N*-H_2CrO_4	21	8
0.05*N*-Oxalic acid	56	21.6
0.05*N*-K_2SO_4+H_2SO_4 (p_H 2.5)	38.6	14

In order to investigate therefore the nature of complication that may arise out of this kind of interactions and to evaluate more definitely the role of aluminium in phosphate adsorption, two samples of ground H-kaolinite, weighing 3.02 g. (I) and 1.35 g. (II), were leached with about 450 ml. of 0.05 *N*-HCl. The leaching was evidently more drastic in the case of the smaller sample. Phosphate adsorption was studied with the original kaolinite, the two samples of ground kaolinite and two samples (I and II) of the ground and acid-treated kaolinite; simultaneously the b.e.c. was also measured. The results are shown in Table V.

TABLE V

B.e.c. and phosphate adsorption of ground kaolinite (KaB).

Material	B.e.c.	PO_4^{3-} adsorbed from 0.05*N*-H_3PO_4.	Al_2O_3 (m.e./100g.). in acid leachate	SiO_2 (m.mol./100g.). in acid leachate	P.a.c. (m.e./100g.).
Original	4	4	...	...	8.2
H-Kaolinite (I) kaolinite, ground (KaB)	10	220	...	...	...
Kaolinite, ground and acid-treated	10	14	223	16	18
(II) Kaolinite, ground (KaB)	8	121	—	...	...
Kaolinite, ground and acid-treated	8	15	221	15	18.5

Ground kaolinite shows increased phosphate adsorption, which is drastically reduced when the ground kaolinite is acid-washed. In the acid leachate considerable amounts of alumina and some amount of silica have been found, indicating the part played by alumina in phosphate adsorption. Both the original and the acid-washed ground kaolinite samples possess somewhat greater b.e.c. and phosphate adsorption, owing evidently to a decrease of particle size. The presence of silica in the acid leachate is indicative of possible disintegration of the kaolinite lattice caused by grinding.

The role of alumina in phosphate adsorption by ground kaolinite also has been shown in the following way.

(*i*) H-kaolinite (KaB) was ground in an agate mortar in presence of *N*-$NH_4H_2PO_4$ solution (p_H 4) and after grinding for 100 hours was washed with aqueous alcohol to make it free from the adhering phosphate. The phosphate taken up by the material was then extracted with *N*-ammonium oxalate (p_H 5). The p.a.c. of the dephosphatised material was then determined.

(*ii*) In another experiment, the same H-kaolinite (KaB) was ground alone in an agate mortar and its p.a.c. was determined by the usual procedure and dephosphatised by leaching with *N*-ammonium oxalate solution (p_H 5). The p.a.c. of the dephosphatised material was again determined. The results of both these experiments are shown in Table VI.

TABLE VI

P.a.c. of ground and dephosphatised kaolinite.

Material.	P.a.c. (m.e./100 g.)	PO_4^{3-} (m.e./100 g.).	Al_2O_3 (m.e./100g.).	SiO_2 (m.mol./100g.).
(*i*) Ground with phosphate	4	322	322	72
(*ii*) Ground without phosphate	61	148	140	7 2

These experiments further suggest a possible breakdown of the mineral by grinding. The above experiments further demonstrate that the reaction with phosphate is more thorough when ground in its presence than when the ground sample is treated with the phosphate solution. Ammonium oxalate dephosphatises the ground sample by removing, more or less specifically, the aluminium phosphate that is formed*. Consequently, the p.a.c. of the dephosphatised sample is considerably reduced. The removal of alumina is almost complete in the first experiment, and hence, the p.a.c. drops to the value of the original unground sample, whereas alumina still present after dephosphatisation in the second sample accounts for its higher p.a.c.

Decomposition of the Lattice of Kaolinite by Phosphate Adsorption

Phosphatisation and subsequent removal of phosphate by ammonium oxalate solution have been shown to cause a slight breakdown of the kaolinite lattice. This is apparently due to the removal of lattice aluminium by combination with phosphate. It is not therefore unlikely that repeated phosphatisation will eventually cause a complete breakdown (Low and Black, *Soil Sci. Soc. Amer. Proc.*, 1947, **12**, 180). The decomposition is considerably enhanced at a higher temperature. For instance, on treatment with N-$NH_4H_2PO_4$ at p_H 4, kaolinite (KaB), which adsorbed only 8.8 m.e. of phosphate at the ordinary temperature, took up nearly 600 m.e. when kept at 95° for 150 hours, the p_H of the solution being raised to 5.7 at the end of the reaction. The phosphatised material on analysis gave 14.9% moisture (105° to ignition), 35.5% SiO_2, 38.3% Al_2O_3 and 11.2% P_2O_5. Assuming that silica is lost as a result of the breakdown of the mineral, it is calculated that nearly 21% of kaolinite has been decomposed in this way. The ratio, $Al_2O_3 : P_2O_5 = 1 : 0.21$, corresponds to variscite, which Cole and Jackson (*J. Phys. Coll. Chem.*, 1950, **54**, 128) also observed by reacting aluminium chloride with phosphate solutions. Compositions other than variscite are, of course, not unlikely.

The use of high temperature, viz. 95°, in the determination of phosphate adsorption capacity of clay and other minerals is therefore not free from objection. This is more so in the case of kaolinite in which there is definite evidence of a chemical reaction and subsequent decomposition. That kaolinite is attacked, though very slowly, even at the ordinary temperature at low p_H, is clearly demonstrated by the data recorded in Table VII. But at p_H 7 the reaction does not seem even at the end of 6 months to proceed further than what occurs in five days.

TABLE VII

Phosphate adsorption by kaolinite over long periods of contact.

Material.	Soln. used.	Period of contact.	Phosphate adsorption (m.e./100 g.). Long period of contact.	5 days' contact.
KaA	0.18N-H_3PO_4 (p_H 4)	Over 5 years	1350	15.0
KaB	N-Ammonium phosphate (p_H 4)	9 months	233	9.0
KaB	N-Ammonium phosphate (p_H 7)	6 months	3.3	3.0

* Table VI clearly shows that the amounts of phosphate and alumina in the ammonium oxalate leachate are nearly equivalent.

Although 58% of the sample (KaA) may be assumed to have reacted with phosphate, no crystallographic evidence of $AlPO_4$ in the X-ray diffraction pattern has been noticed. Electron diffraction pictures* of KaB, before and after dephosphatisation with *N*-ammonium oxalate solution, have shown definite rings, besides those for kaolinite, corresponding to a new compound which could not be identified in the phosphatised sample; the rings disappeared on dephosphatisation. The dephosphatised mineral was the original kaolinite so far as electron diffraction pattern was concerned.

From the above discussion of the results it is quite clear that phosphate adsorption, or anion exchange, in general, by kaolinites is rendered complicated by the presence of aluminium, either in the free state or present in the laterally broken down lattice. The actual condition can be assessed if the contribution due to aluminium is taken into account. For instance, the very much increased adsorption of phosphate by ground kaolinite has been shown to be due mainly to aluminium, but not to any real increase in the adsorption capacity of kaolinite itself. Accordingly, the phosphate adsorption capacity of kaolinite becomes very low, of the order of 3-4 m.e. per 100 g., which is also the b.e.c. of unground kaolinite. The agreement between the anion exchange or phosphate adsorption capacity of kaolinite and its base exchange capacity has been explained by assuming that the surface OH groups act as the centre of both cation and anion exchange, depending on the experimental conditions (Marshall, "Colloid Chemistry of Silicate Minerals", 1949, Academic Press, N. Y.).

Halloysite

Only a few experiments could be carried out with the halloysite fraction ($< 2\mu$). The results are shown in Table VIII.

TABLE VIII

Adsorption of ions by halloysite ($< 2\ \mu$).

Solution.	Adsorption (m.e./100 g.)**	
N-Barium acetate (p_H 7)	4.8 ...	(b.e.c.)
N-Ammonium phosphate (p_H 7)	8.2 ...	(phosphate)
N-Ammonium phosphate (p_H 4)	151 ...	(p.a.c.)
N-Ammonium phosphate (p_H 7) †	61 ...	(phosphate)

* Kindly taken by Prof. R. P. Mitra while at the Imperial College of Science and Technology, London.

** On air-dry sample.

† At 90°-95° for 100 hrs.

The b. e. c. is almost the same as that of kaolinite, but the phosphate adsorption capacity is higher at both p_H's, particularly in the acidic solution. The influence of temperature is also similar to kaolinite. But halloysite appears to be somewhat more reactive than kaolinite so far as phosphate interaction is concerned. This is possibly due to the comparatively open lattice tructure of halloysite.

Thanks of the author are due to Dr. S. K. Mukherjee of the Department of Applied Chemistry, University College of Science and Technology, Calcutta.

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Received July 18, 19 5.

[Jour. Indian Chem. Soc., Vol. 33, No. 6, 1956]

BENZYLTHIOUREAS. PART I

By (Late) J. H. Shah, J. P. Trivedi and J. J. Trivedi

Several mono- and N : N'-disubstituted benzylthioureas have been prepared for studying their biological properties.

Substituted thioureas show a wide variety of physiological activity, thus : 4 : 4-dialkoxythiocarbanilides show tuberculostatic properties (Huebner, *J. Amer. Chem. Soc.*, 1953, **75**, 2274) and are also active against human leprosy (Buu-Hoï, *Internat. J. Leprosy*, 1951, **22**, 16). Certain diarylthioureas have been found active against influenza-virus infections in mice (Buu-Hoï *et al.*, *Compt. rend.*, 1954, **238**, 2582). Some arylthioureas have been reported to exhibit anthelmintic activity (Shimotani, *J. Pharm. Soc. Japan*, 1952, **72**, 328). Benzylthiourea shows antithyroid activity (Rascova, *Casopis Lèkárů C'eskych*, 1947, **86**, 979).

With a view to studying their physiological properties, several substituted benzylthioureas have been prepared from substituted benzylamines through the corresponding *iso*thiocyanates, either by the action of ammonia or the appropriate amine.

Compounds 1 to 7 (Table II), when tested by the agar plate method, were found to show bacteriostatic activity against *Staphylococcus citrus*, *Staph. albus*, *Staph. aureus*, *Bacillus subtilis* and Typhus. Details will be published elsewhere.

Experimental

Substituted benzylamines were prepared from the corresponding substituted benzyl halides by the method of Graymore (*J Chem. Soc.*, 1947, 1116).

Following the procedure described in "Organic Synthesis" (Vol. **21**, p. 81) the substituted benzylamines were converted into the corresponding substituted benzyl *iso*thiocyanates in yields varying from 50% to 70% (vide Table I).

Table I

$X\text{-}C_6H_4CH_2\text{-}N=C=S$.

Compounds. X=	B.P.	* *D.*	* Ref. index.	Formula.	Found. X%.	Found. S%.	Calc. X%.	Calc. S%.
1. *o*-Cl	138°/6 mm.	1.203	1.5788	C_8H_6NClS	19 3	17.4	19.3	17.5
2. *m*-Cl	140°-45°/6	1.201	1.5784	,, ,,	19 3	17.4	,, ,,	,, ,,
3 *p*-Cl	130-33°/4	1.206	1.5698	,, ,,	19 2	17.4	,, ,,	,, ,,
4 *o*-Br	130-34°/5	1.403	1.6048	C_8H_6NBrS	35.0	14 0	35.0	14.1
5. *m*-Br	147°/5	1.503	1 6384	,, ,,	35.0	14.0	,, ,,	,, ,,
6. *p*-Br	140-44°/5-7	1.381	1 6037	,, ,,	34.9	13.9	,, ,,	,, ,,
7. *p*-I	167°/3-4	1.521	1.6088	C_8H_6NIS	46.1	11.7	46.1	11.6
8. *m*-I	162°/3-4	1.667	1.6170	,, ,,	46 0	11 6	,, ,,	,, ,,

* Density and refractive index (sodium light) were determined at 27°.

Following the same method as above, mono-substituted thioureas were prepared in quantitative yields by the action of ammonia on substituted benzyl *iso*thiocyanates. N : N'-disubstituted thioureas were prepared in quantitative yields by the action of

primary amines on the substituted benzyl *iso*thiocyanates using the method of Kaye and Parris (*J. Org. Chem.*, 1951, **16**, 1862). Mono- and N : N′-disubstituted thioureas prepared are shown in Tables II and III respectively. Thioureas crystallised from hot water or alcohol usually in needles.

TABLE II

$X\text{-}C_6H_4CH_2\text{-}NHCSNH_2$.

Substance. X=	M.P.	Formula.	Found.		Calc.	
			X%	S%	X%	S%
1. *o*-Cl	126°	$C_8H_9N_2ClS$	17.6	16.0	17.7	15.9
2. *m*-Cl	133°	" "	17.6	15.9	" "	" "
3. *p*-Cl	141°	" "	17.6	15 9	" "	" "
4. *o*-Br	127°	$C_8H_9N_2BrS$	32.6	13 0	32.6	13.1
5. *m*-Br	151°	" "	32.6	13 1	" "	" "
6. *p*-Br	157°	" "	32.5	13 1	" "	" "
7. *p*-I	162-64°	$C_8H_9N_2IS$	43.4	11.0	43.4	10.9
8. *m*-I	151°	" "	43.4	10.9	" "	" "

TABLE III

$X\text{-}C_6H_4CH_2\text{-}NHCSNH\text{-}R$.

Substance. X=	R=	M.P	Formula.	Found.		Calc.	
				X%	S%.	X%	S%
9. *o*-Cl	$-CH_2C_6H_5$	165°	$C_{15}H_{15}N_2ClS$	12.2	11.0	12.2	11.0
10. *m*-Cl	" "	84°	" " "	12.2	11.1	"	"
11. *p*-Cl	" "	140°	" " "	12.2	11.0	"	"
12. *o*-Br	" "	100°	$C_{15}H_{15}N_2BrS$	23 8	9.5	23.8	9.6
13. *m*-Br	" "	90°	" " "	23 8	9 5	"	"
14. *p* Br	" "	139°	" " "	23.8	9.6	"	"
15. *p*-I	" "	103°	$C_{15}H_{15}N_2IS$	33.2	8 4	33.2	8.4
16. *o*-Cl	α-$C_{10}H_7$	157°	$C_{18}H_{15}N_2ClS$	10.8	9.8	10.9	9.8
17. *m*-Cl	" "	124°	" " "	10.8	9.8	"	"
18. *p*-Cl	" "	143°	" " "	10.8	9.8	"	"
19. *o*-Br	" "	163°	$C_{18}H_{15}N_2BrS$	21.5	8.6	21.5	8 6
20. *m*-Br	" "	129°	" " "	21.5	8.7	"	"
21. *p*-Br	" "	157°	" " "	21.5	8 6	"	"
22. *p*-I	" "	166°	$C_{18}H_{15}N_2IS$	30.3	7 6	30.3	7.7
23. *m*-I	" "	156°	" " "	30.3	7.6	"	"
24. *o*-Cl	β-$C_{10}H_7$	160°	$C_{18}H_{15}N_2ClS$	10.8	9 8	10.9	9.8
25. *m*-Cl	" "	153°	" " "	10.8	9.8	"	"
26. *p*-Cl	" "	169°	" " "	10.8	9.7	"	"
27 *o*-Br	" "	161°	$C_{18}H_{15}N_2BrS$	21.-	8.6	21.5	8.6
28. *m*-Br	" "	163°	" " "	21.5	8.6	21.5	8.6
29. *p*-Br	" "	173°	" " "	21 5	8.6	"	"
30. *p*-I	" "	180°	$C_{18}H_{15}N_2IS$	30.3	7.6	30.3	7.7
31. *m*-I	" "	172°	" " "	30.2	7.6	"	"

The authors thank the Ahmedabad Education Society for facilities and the Principal Dr. R.D. Desai for interest in the work.

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Received October 8, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 6, 1956]

HETEROCYCLIC COMPOUNDS. PART XXIX. THE SYNTHESIS OF SUBSTITUTED 1-METHYL- AND 3-METHYL-1 : 2 : 3 : 4-TETRAHYDROACRIDONES

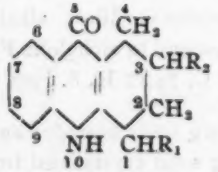
By R. D. Desai and D. V. Shintre

1-Methyl-, 2-methyl- and 3-methyl-1 : 2 : 3 : 4-tetrahydro-5-acridones have been prepared from aniline and ethyl 6 methyl-, 5-methyl- and 4-methyl*cyclo*hexan-1-one-2-carboxylates by the method of Conrad and Limpach. The tetrahydroacridones have been converted into their 5-chloroacridines for identification. The substituted derivatives of 1-methyl- and 3-methyltetrahydroacridones containing the substituents in the unreduced benezene ring have been prepared by condensing *o*- and *p*-toluidines, *o*- and *p*-anisidines, and *o*- and *p*-phenetidines with the corresponding cyclic β-ketonic esters and have been converted into their corresponding 5-chloroacridines.

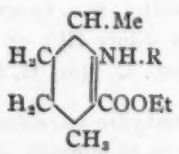
Though 1 : 2 : 3 : 4-tetrahydro-5-acridones (I: $R_1=R_2=H$, hereafter called tetrahydroacridones) with substituents in the benzene ring are fairly well known, the number of those with the substituents in the reduced benzene ring is very small. Thus, Perkin and Sedgwick (*J. Chem. Soc*, 1924, **125**, 2437) prepared 2-methyltetrahydro-5-acridone from *o*-aminobenzoic acid and 3-methyl*cyclo*hexanone, while Dasgupta and Basu (this *Journal*, 1937, **14**, 468) prepared 2-methyl-7-chloro- and 2-methyl-7-methoxy-tetrahydro-5-acridones from ethyl 5-methyl*cyclo*hexan-1-one-2-carboxylate and *p*-chloroaniline and *p*-anisidine by the method of Conrad and Limpach (*Ber.*, 1887, **20**, 944). Buksh and Desai (*Proc. Ind. Acad. Sci.*, 1939, **10A**, 262) prepared 1-methyl- and 3-methyltetrahydroacridones by the application of Borche and Tiedke's method (*Ber.*, 1908, **41**, 220 ; 1909, **42**, 624).

In continuation of our previous work (*loc. cit.*) we have taken up the systematic investigation of the synthesis of some simple tetrahydroacridones with substituents in the reduced ring by the method of Conrad and Limpach.

Ethyl 6-methyl*cyclo*hexan-1-one-2-carbaxylate was condensed with aniline, *o*- and *p*-toluidines, *o*- and *p*-anisidines, *o*- and *p*-phenetidines at the room temperature by the method of Coffey, Thompson and Wilson (*J. Chem. Soc.*, 1936, 856). The resulting ethyl 1-arylamino-$\Delta^{1:2}$-6-methyl*cyclo*hexene-2-carboxylates (II) were cyclised by heating at 240°-250° to their respective 1-methyltetrahydro-5-acridones (I: $R_1=Me$; $R_2=H$).



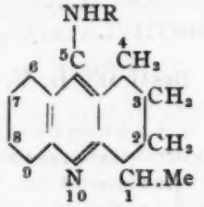
(I)



(II)
[R = phenyl, *o*-tolyl, *p*-tolyl, *o*-methoxyphenyl etc.]

By heating with a mixture of phosphorus pentachloride and phosphorus oxychloride the tetrahydro-5-acridones were converted into their corresponding tetrahydro-5-chloro-

acridines, some of which were further characterised as anilino, *p*-toluidino and piperidino derivatives (III : R = phenyl or *p*-tolyl or piperidyl).



(III)

As some of the tetrahydroacridones have high m.p., these 5-chloroacridines or their arylamino derivatives, which have low melting points are useful for their identification.

Ethyl 4-methyl*cyclo*hexan-1-one-2-carboxylate has been condensed with arylamines, mentioned above, and the resulting arylamino-4-methyl*cyclo*hexene-2-carboxylates have been cyclised to 3-methyltetrahydro-5-acridone derivatives (I : R_1 = H ; R_2 = Me). These have been converted into the corresponding 3-methyltetrahydro-5-chloroacridines and 3-methyltetrahydro-5-arylaminoacridines. The work on the condensation of these aryl*cyclo*hexanone-2-carboxylates with amines at high temperatures and the conversion of the resulting anilides to the corresponding phenanthridones will be published in a later communication. The work described in this paper was completed twelve years ago, but owing to unavoidable circumstances the publication was delayed.

Experimental

Ethyl 1-Anilino-$\Delta^{1:2}$*-6-methylcyclohexene-2-carboxylate* (II : R = Ph).—A mixture of aniline (9.3 g.), ethyl 6-methyl*cyclo*hexan-1-one-2-carboxylate (18.4 g.) and HCl (conc., 0.5 c.c.) was kept for 48 hours in a vacuum desiccator. The solid mass was washed with a small amount of petrol (b.p. 45°-50°) and the residue crystallised from rectified spirit in short needles, m.p. 95-96°, yield 80%. It is insoluble in dilute alkali solution, but dissolves in dilute HCl on warming and does not respond to alcholic $FeCl_3$ colour reaction. (Found : C, 74.0; H, 8.3. $C_{16}H_{21}O_2N$ requires C, 74.1; H, 8.1 per cent).

1-Methyltetrahydro 5-acridone.—The above solid (13.0 g.) was heated in an oil-bath at 240°-250° for 20 to 25 minutes, and cooled. The resulting solid crystallised from benzene in small, lustrous plates, m.p. 344-45°, yield 70%. It is soluble in hot dilute mineral acids, hot dilute alkali, but insoluble in sodium carbonate solution. It was identical in m.p. and mixed m.p. with a specimen prepared by Baksh and Desai (*loc. cit.*) from anthranilic acid and *O*-methyl*cyclo*hexanone. (Found : C, 78.7 ; H, 7.1. Calc. for $C_{14}H_{15}ON$: C, 78.9 ; H, 7.0 per cent).

TABLE I

M = methyl*cyclo*hexene-2-carboxylate. *T* = 1 : 2 : 3 : 4-tetrahydro-5-acridone. T_1 = 1 : 2 : 3 : 4-tetrahydro-5-chloroacridine.

Compounds.	Formula.	Crystalline form.	M.P.	Analysis. Found.	Analysis. Calc.
1. 1-*p*-Toluidino-$\Delta^{1:2}$-6-M.	$C_{17}H_{23}O_2N$ (80%)	Needles from alcohol.	119°	C: 74.7% H: 8.4	74.7% 8.4
2. 1 :7-Dimethyl-T.	$C_{15}H_{17}ON$ (85%)	Colorless prisms. *	268°	C: 79 2 H: 7 6	79.3 7.5
3. 1 :7-Dimethyl-T_1.	$C_{15}H_{16}NCl$	Prisms from alcohol.	87°	Cl: 14.6	14.5
4. 1-*o*-Toluidino-$\Delta^{1:2}$-6-M.	$C_{17}H_{23}O_2N$ (60%)	Needles from hexane.	134°	C: 74.8 H: 8.3	74.7 8.4
5. 1 :9-Dimethyl-T.	$C_{15}H_{17}ON$ (52%)	Needles from alcohol.	296°	C: 79.5 H: 7.4	79.3 7.5
6. 1 :9-Dimethyl-T_1.	$C_{15}H_{16}NCl$	Small needles from petrol.	72°	Cl: 14.6	14.5
7. 1-*p*-Anisidino-$\Delta^{1:2}$-6-M.	$C_{17}H_{23}O_3N$ (50%)	Needles from alcohol.	92°	C: 70.4 H: 8.1	70.6 8.0
8. 1-Methyl-7-methoxy-T.	$C_{15}H_{17}O_2N$	Do	257°	C: 73 9 H: 7.2	74.0 7.0
9. 1-Methyl-7-methoxy-T_1.	$C_{15}H_{16}ONCl$	Prisms from alcohol.	81°	Cl: 13.8	13.6
10. 1-*o*-Anisidino-$\Delta^{1:2}$-6-M.	$C_{17}H_{23}O_3N$ (30%)	Needles from benzene.	89-90°	C: 70 4 H: 8.2	70.6 8 0
11. 1-Methyl-9-methoxy-T.	$C_{15}H_{17}O_2N$ (20%)	Needles from alcohol.	274°	C: 73.8 H: 6.9	74.0 7.0
12. 1-Methyl-9-methoxy-T_1.	$C_{15}H_{16}ONCl$	White needles from alcohol.	98-99°	Cl: 13 7	13.6
13. 1-*p*-Phenetidino-$\Delta^{1:2}$-6-M.	$C_{18}H_{25}O_3N$ (65%)	Plates from alcohol	109-110°	C: 71.1 H: 8.2	71.3 8.3
14. 1-Methyl-7-ethoxy-T.	$C_{16}H_{19}O_2N$	Do	>300°	C: 74.7 H: 7.4	74.7 7.3
15. 1-Methyl-7-ethoxy-T_1.	$C_{16}H_{18}ONCl$	Yellow needles from pet. ether.	92°	Cl: 13.0	12.9
16. 1-*o*-Phenetidino-$\Delta^{1:2}$-6-M.	$C_{18}H_{25}O_3N$ (50%)	Prisms from hexane.	114°	C: 71.2 H: 8.4	71.3 8.2
17. 1-Methyl-9-ethoxy-T.	$C_{16}H_{19}O_2N$	Colorless needles from alcohol.	251°	C: 74.6 H: 7.5	74.7 7.3
18. 1-Methyl-9-ethoxy-T_1.	$C_{16}H_{18}ONCl$	Small prisms from alcohol.	100°	Cl: 13.1	12.9

* Figures in parenthesis denote % yield.

TABLE II

3-Methyltetrahydro-5-acridone and its derivatives.

	Compounds.	Formula.	Crystalline form.	M.P.	Analysis, Found.	Calc.
1.	1-Anilino-$\Delta^{1:2}$-4-M.	$C_{16}H_{21}O_3N$ (80%)	Lustrous prisms from alcohol.	106-107°	C: 74.2%	74.1%
					H: 8.0	8.1
2.	3-Methyl-T.	$C_{14}H_{15}ON$ (95%)	Plates from alcohol.	>350°	C: 78.7	78.8
					H: 7.0	7.0
3.	3 Methyl-T_1.	$C_{14}H_{14}NCl$ (80%)	Yellowish plates from hexane.	64°	Cl: 15.4	15.3
4.	5-Anilino der. of (3).	$C_{20}H_{20}N_2$ (80%)	Pale yellow plates from benzene.	186°	N: 9.6	9.7
5.	5 *p*-Toluidino der of (3).	$C_{21}H_{22}N_2$ (70%)	Yellow plates from benzene.	146°	N: 9.1	9.3
6.	5-Piperidino der. of (3).	$C_{19}H_{24}N_2$ (30%)	Orange needles from benzene.	151°	N: 9.7	10.0
7.	1-*p*-Toluidino-$\Delta^{1:2}$-4-M.	$C_{17}H_{23}O_2N$ (75%)	Leaflets from benzene.	126°	C: 74.7	74.7
					H: 8.6	8.4
8.	3:7-Dimethyl-T.	$C_{15}H_{17}ON$ (85%)	Plates from alcohol.	>310°	C: 79.1	79.3
					H: 7.5	7.5
9.	3:7-Dimethyl T_1.	$C_{15}H_{16}NCl$ (85%)	Prisms from alcohol.	88°	Cl: 14.7	14.5
10.	1-*o*-Toluidino-$\Delta^{1:2}$-4-M.	$C_{17}H_{23}O_2N$ (60%)	Colorless plates from hexane.	121°	C: 74.6	74.7
					H: 8.5	8.4
11.	3:9-Dimethyl-T.	$C_{15}H_{17}ON$,,	Microscopic plates from alcohol.	279°	N: 6.0	6.2
12.	3:9-Dimethyl T_1.	$C_{15}H_{16}NCl$ (70%)	Yellow plates from hexane.	52°	Cl: 14.6	14.5
13.	1-*p*-Anisidino-$\Delta^{1:2}$-4-M.	$C_{17}H_{23}O_3N$,,	Needles from hexane.	85°	C: 70.3	70.6
					H: 8.2	8.0
14.	3-Methyl-7-methoxy-T.	$C_{15}H_{17}O_2N$ (80%)	Microcrystals from alcohol.	288°	C: 73.9	74.1
					H: 7.1	7.0
15.	3-Methyl-7-methoxy-T_1.	$C_{15}H_{16}ONCl$ (50%)	Small needles from alcohol.	113°	Cl: 13.4	13.6
16.	1-*o*-Anisidino-$\Delta^{1:2}$-4-M.	$C_{17}H_{23}O_3N$ (63%)	Thick plates from hexane.	99°	C: 70.2	70.6
					H: 8.0	8.0
17.	3-Methyl-9-methoxy-T.	$C_{15}H_{17}O_2N$ (55%)	Small plates from alcohol.	235°	C: 73.9	74.1
					H: 7.2	7.0
18.	3-Methyl-9-methoxy-T_1.	$C_{15}H_{16}ONCl$	Plates from hexane.	86°	Cl: 13.7	13.6
19.	1-*p*-Phenetidino-$\Delta^{1:2}$-4-M.	$C_{18}H_{25}O_3N$ (60%)	Prismatic needles from alcohol.	129°	C: 71.0	71.3
					H: 8.3	8.2
20.	3-Methyl-7-ethoxy-T.	$C_{16}H_{19}O_2N$ (65%)	Needles from alcohol.	>320°	C: 74.5	74.7
					H: 7.5	7.3
21.	3-Methyl-7-ethoxy-T_1.	$C_{16}H_{18}ONCl$ (70%)	Needles from hexane.	117°	Cl: 12.7	12.9
22.	1-*o*-Phenetidino-$\Delta^{1:2}$-4-M.	$C_{18}H_{25}O_3N$ (65%)	Lustrous flakes from hexane.	137°	C: 71.1	71.3
					H: 8.0	8.2
23.	3-Methyl-9-ethoxy-T.	$C_{16}H_{19}O_2N$ (50%)	Prismatic needles from alcohol.	293°	C: 74.4	74.7
					H: 7.2	7.3
24.	3-Methyl-9-ethoxy-T_1.	$C_{16}H_{18}ONCl$ (70%)		107°	Cl: 12.8	12.9
25.	1-Anilino-$\Delta^{1:2}$-5-M.	$C_{16}H_{21}O_2N$ (70%)	Tiny plates from alcohol.	98°	C: 74.2	74.1
					H: 8.0	8.1
26.	2-Methyl-T.	$C_{14}H_{15}ON$ (60%)		342°	C: 78.9	78.8
					H: 6.9	7.0

1-Methyltetrahydro-5-chloroacridine.—A mixture of 1-methyltetrahydroacridine (2.1 g.), PCl_5 (2.0 g.) and $POCl_3$ (3.0 c.c.) was heated for 1½ hours at 120°-130°, after the vigorous initial reaction had subsided. After removal of $POCl_3$, the contents were decomposed by ice-cold water when an almost clear solution was obtained. The clear filtrate was made alkaline with dilute ammonia when a flocculent yellow precipitate was obtained. It crystallised from petrol (b.p. 50°-60°) in pale yellow thick plates, m.p. 76°, yield 70%. The chloroacridine dissolved in dilute HCl with a faint green fluorescence. (Found : Cl, 15.4. $C_{14}H_{14}NCl$ requires Cl, 15.3 per cent).

1-Methyltetrahydro-5-anilinoacridine (III : R = Ph).—A mixture of the above 1-methyltetrahydro-5- chloroacridine (1.2 g.), aniline (0.5 g.) and freshly precipitated copper (0.05 g.) was heated in a hard-glass tube at 170°-180° for 10 hours. The resulting solid was washed with ether, and dissolved in water. On the addition of dilute ammonia solution, the base was obtained as a yellow solid which crystallised from benzene in long yellow needles, m.p. 193-94°, yield 65%. It is easily soluble in alcohol as well as in dilute HCl. (Found : N, 9.6. $C_{20}H_{20}N_2$ requires N, 9.7 per cent).

1-Methyltetrahydro-5-toluidinoacridine, similarly prepared from 1-methyltetrahydro-5-chloroacridine (1.2 g.) and *p*-toluidine (0.6 g.), crystallised from benzene in lustrous yellow leaflets, m.p. 157-58°, yield 75%. (Found : N, 9.1. $C_{21}H_{22}N_2$ requires N, 9.2 per cent).

1-Methyltetrahydro-5-piperidinoacridine was similarly obtained from the 1-methyltetrahydro-5-chloroacridine (1.2 g.) and piperidine (1.7 g.) and crystallised from benzene in orange-yellow leaflets, m.p. 137-38°, yield 45%. (Found : N, 9.7. $C_{19}H_{24}N_2$ requires N, 10.0 per cent).

As the experimental details of the condensation of *o*-toluidine, *o*-anisidine, *o*-phenetidine, *p*-toluidine, *p*-anisidine and *p*-phenetidine with ethyl 6-methyl*cyclo*hexan-1-one-2-carboxylate and the preparation of other derivatives are similar to those described of aniline, their physical and chemical properities are only listed in Table I.

The experimental details of the condensation of ethyl 4-methyl*cyclo*hexan-1-one-2-carboxylate with various amines, their cyclisation to 3-methyltetrahydro-5-acridones and the conversion of the latter into 3-methyltetrahydro-5-chloroacridines are similar to those of ethyl 6-methyl*cyclo*hexan-1-one-2-carboxylate. The results are listed in Table II, which also includes the synthesis of 2-methyltetrahydro-5-acridone from ethyl 5-methyl*cyclo*hexane-1-one-2-carboxylate and aniline (25 and 26), though it has been prepared by Borsche and Tiedke's method by Perkin and Sedgwick.

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Received September 6, 1955

[Jour. Indian Chem. Soc., Vol. 33, No. 6, 1956]

INTERACTION OF RUBBER AND CARBON TETRACHLORIDE

By J. B. Pande, D. Raghunath and C S. Ramakrishnan

A mechanism for the evolution of hydro en chloride due to interaction of rubber and carbon tetrachloride, when brought together in direct sunlight, diffused daylight or to radiations of wave-lengths about and below 5200Å, is suggested

Carbon tetrachloride has been used for studies on the solution properties of natural rubber. It has been tacitly assumed that no chemical reaction between the two takes place; but carbon tetrachloride has been found to show a negative heat of mixing with natural rubber. There is absorption of heat (0.37-1.36 cal./g.) with benzene, dichloroethylene and toluene, while there is evolution of heat (2-3 cal./g.) with carbon tetrachloride and chloroform (Hock and Schmidt, *Rubber Chem. Tech*, 1934, 7, 462; cf. "Advances in Colloid Science", Vol. II, Interscience, 1946, p. 155). There is considerable evolution of heat ("Natural & Synthetic High Polymers", Vol. IV, Interscience, 1950, p. 704) on mixing cellulose triacetate with tetrachloroethane and the solvent is found to be completely bound with the polymer. It appears therefore that similar combination between rubber and carbon tetrachloride may occur, when these are brought together. An indication of chemical interaction of carbon tetrachloride and rubber has been found in an examination of the spectra of carbon tetrachloride solutions of natural rubber (Dasgupta, Ramakrishnan and Pande, *J. Polymer Sci.*, 1955, **17**, 255). Chemical analysis of rubber, aged in solution at the laboratory temperature, showed that chlorine was incorporated into the rubber.

In the present investigation a progressive detailed study of the system of deproteinised rubber-carbon tetrachloride has been carried out from the instant the two are brought in contact till either a homogeneous solution (in darkness only) or a gel is obtained (visible radiations).

Experimental

Deproteinised natural rubber (about 0.2 g.) was accurately weighed. An amount of CCl_4 that would furnish a 2% (w/v) solution was taken in a pyrex tube (20 c.c.) having a ground-glass joint. The weighed rubber was added under the conditions of experiment and the tube closed with another pyrex tube (20 c.c.) with a reciprocal ground-glass joint. The opposite end of this second tube had earlier been drawn out into a capillary and sealed. For the experiments with diffused daylight and direct sunlight, the tubes were exposed on racks. In experiments with different wavelengths of light, the tubes were mounted on a water-cooled panel opposite 'Baker' 2" × 2" filters and placed about 10" away and equidistant from a 200 watt clear tungsten lamp. Experiments were also carried out in which samples were mixed and kept in complete darkness.

After the exposure, the capillary was broken under water, when water rushed into the tubes. The contents of the tubes were refluxed for fifteen minutes and the hydrogen chloride determined. The chlorine content of the rubber left from refluxing was determined after precipitation with methyl alcohol, followed by solution in benzene and reprecipitation with methyl alcohol.

TABLE I

A. Direct sunlight in pyrex tube.

Exposed for (in hrs.)	...	12	24	48	60	96	168	1980
% Free HCl on wt. of rubber	...	0.4	1.4	1.5	2.2	2.4	3.3	7.1
%Cl content of the rubber	...	1.5	3.3	4.3	6.7	...	9-12	31 0

B. Diffused daylight in pyrex tube.

Exposed for (in hrs.)	...	12	24	36	84	108
% Free HCl on wt. of rubber	...	0.2	0.3	0.6	0.9	1.2
%Cl content of rubber	...	1.3	1.2	2.0	2.8	3.94

TABLE II

Nature of tube.	Time of exposure.	Nature of exposure.	% Free HCl on wt. of rubber.	%Cl content of the rubber.
Pyrex	96 hrs.	Red filter, 6500Å	0.0	0.0
,,	96	Yellow filter 5800Å	0.0	0.0
,,	96	Dark green filter 5200Å	0.0096	0.0
,,	96	Dark blue, 4700Å	0.076	0.71
Quartz	15½	U.V. 3600Å	0.69	2.5
,,	36	U.V. 3600Å	1.59	6 5

DISCUSSION

It is observed (Table I) that evolution of HCl progressively increases and attains a a value of 7% in 1980 hours of exposure in direct sunlight; exposure to diffused daylight also gives off HCl which attains a value of 1.2% in 108 hours. There is a simultaneous incorporation of chlorine as well. It has been found possible to attain as high a chlorine content as 31% on prolonged exposure to sunlight.

Table II shows that hydrogen chloride is evolved when the samples are exposed to radiations of wave-lengths about and below 5200Å, chlorination of rubber also taking place simultaneously. Such reactions also take place when rubber —CCl_4 systems are exposed in a quartz tube to U.V. radiation (3600Å).

In samples which were mixed and kept in complete darkness there was no hydrogen chloride evolution.

These results show that CCl_4— rubber systems progressively pass on into partially chlorinated rubber —CCl_4 systems, with evolution of HCl unless they are kept in complete darkness or exposed only to light of wave-lengths above 5200 Å.

This observation throws doubt on the validity of the results of solution properties of rubber —CCl_4 systems, reported in literature, since a part of the rubber would have changed into chlorinated rubber. Hock and Schmidt (*loc. cit.*) observed a negative heat of solution when rubber was dissolved in CCl_4. The evolution of HCl during this dissolution process explains this negative heat of solution.

Kharasch, Jensen and Urry (*J. Amer. Chem. Soc.*, 1947, **69**, 1100) have shown that mono-olefins, such as octene-1, react with CCl_4 only in presence of peroxides or ultraviolet light, these being responsible for the splitting of CCl_4 into radicals. They do not report the evolution of HCl by a substitutive attack of the free radicals on the olefin. The absence of a chemical reaction between rubber and CCl_4 in the dark suggests that peroxidic centres, even if present in unmasticated deproteinised rubber, are not responsible for this reaction. Bateman (*J. Polymer Sci.*, 194 , **2**, 1) has shown that photodecomposition of natural rubber takes place only when rubber is irradiated with ultraviolet light. That photodissociation of CCl_4 does not take place with visible radiation can be judged from the fact that its absorption continiuum has been reported to be in the ultraviolet region (2800 Å to 2700Å) (Saha, *Bull. Acad. Sci.*, U.P., 1933, **2**, 233; Lowry and Sass, *J. Chem. Soc.*, 1926, 622). The fact that hydrogen chloride is evolved under conditions, which normally exclude the decomposition of either rubber or CCl_4, suggests that rubber-CCl_4 systems give rise to hydrogen chloride and chlorinated rubber even at lower energy levels by absorption of light of wave-lengths between 3000Å and 5200Å. Results in Table II indicate that at energy levels lower than that corresponding to 5200Å no chemical change takes place, as revealed by the absence of HCl.

The following explanations are offered for the observations on the interaction of rubber and CCl_4 even with radiations of longer wave-length.

Transference of high energy through marco-molecules has been suggested by Alexander and Charlesby (*Nature*, 1954, **173**, 4404, 578) to explain the particular behaviour of various polymers under the action of high energy radiation. In the present investigation reactions requiring normally a higher energy, viz., photodecomposition of either rubber or carbon tetrachloride to furnish radicals, are brought about in this macromolecular system by the absorption and transference of lower energies.

From an examination of the infra-red spectrum of CCl_4 solutions of natural rubber (*loc. cit.*) it has been postulated that a complex is formed between the two. It is also possible that even the low energies corresponding to 5200 Å, absorbed in various parts of the rubber chain, result in the decomposition of the complex to provide radicals, which then chlorinate the rubber and at the same time, to some extent, react substitutively, giving off hydrogen chloride.

The authors wish to express their thanks to the Director, National Chemical Laboratory of India, Poona, for permission to publish the results and to Dr. S.L. Kapur for his interest.

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Received June 2, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 6, 1956]

BERYLLIUM FLUORIDES. PART I. STUDIES ON HYDROLYSIS OF FLUOBERYLLATE ION (BeF_4^{2-}) BY CONDUCTIVITY AND THERMOMETRY

By Apurba Kumar Sen Gupta

By conductivity, thermometry and chemical methods it has been shown that the primary reaction between caustic soda and fluoberyllate ion occurs according to the equation : $BeF_4^{2-} + 2OH^- = Be(OH)_2 + 4F'$; the secondary reaction, *i.e.* the dissolution of $Be(OH)_2$ in excess of alkali, occurs subsequently, forming beryllate ion ; no indication of the formation of $[BeF_3OH]^{2-}$ has been found.

The fluoberyllates of alkali metals were known from the time of Marignac (*Ann. chim. phys.*, 1873, *iv*, **30**, 45). Previously these compounds were regarded as double salts of alkali metal fluorides and beryllium fluoride. The identity of BeF_4^{2-} as a complex anion and its isomorphism with SO_4^{2-} ion were recognised and established by Sarkar and Rây (this *Journal*, 1929, **6**, 987) and Rây (*Z. anorg. allg. Chem.*, 1931, **201**, 289).

Recently Mitra (this *Journal*, 1955, **32**, 241) published his thermometric studies on the hydrolysis of BeF_4^{2-}. As the data published by Mitra are incomprehensible from the light of the work done by the present author, the results, obtained by the author, are recorded in this communication along with the data that have been found by repeating the experiment with the same quantities of substances recorded by Mitra (*loc. cit.*).

Experimental

Potassium fluoberyllate was prepared in the conventional way from freshly precipitated $Be(OH)_2$ and adding a slight excess of KHF_2 to the required amount. It was recrystallised from water and washed with water and alcohol. After drying in an air-oven at 110°, it was analysed by standard methods for fluorine and found to conform to the formula K_2BeF_4. Other reagents used were of A. R. quality.

The conductivities of solutions were measured by Philips' conductivity measuring bridge, type GM 4249. The conductivity vessel consisted of a polyethylene beaker. The glass stems of the two platinised electrodes were carefully covered with wax. Potassium fluoberyllate solution was taken in the beaker and caustic soda solution was added from a burette ; the solution was stirred with a plastic rod. Curves I and II (Fig. 1) show the conductometric titration results. The change of conductance after each addition was plotted against respective volumes of caustic soda solution added.

The thermometric titration set up was fitted according to Dutoit (*J. chim. phys.*, 1921, **19**, 324) and titration was done taking all the precautions as laid down by him. Potassium fluoberyllate solution was taken in the Dewar flask and caustic soda solution was added from a burette. The change in temperature after each addition of alkali was noted with a Beckmann thermometer. The thermometric titration results are represented in curves III, IV and V (Fig. 2). In curves III and IV the total change

of temperature, $(T-T_0)$, was plotted against the volume of caustic soda solution added. Curve V was obtained with the same data of curve III after making volume correction according to Chatterjee (this *Journal*, 1955, **32**, 366) ; in this curve total temperature change for a constant volume,

$$(T-T_0)\times(V_0+\Delta V)/V_0$$

was plotted against the volume of caustic soda solution added. Curve IV represents the data obtained by repeating with the quantities of K_2BeF_4 and NaOH recorded by Mitra (*loc.cit.*). As was written by him, the solution of K_2BeF_4 was made by shaking in minimum volume of water (approx. 90 c.c.) in a 100 c.c. volumetric flask and was transferred into the Dewar flask. The volumetric flask was washed several times with small amounts of water and the washings were added to the Dewar flask. As the exact volume of K_2BeF_4 solution after the dilution was not known, similar curve like the curve V could not be drawn with the data of curve IV.

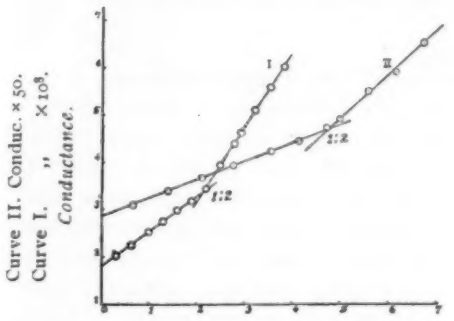
For investigating the formation of K_2BeF_3OH (as suggested by Mitra, *loc. cit.*, during the addition of NaOH to K_2BeF_4), 0.4804 g. of K_2BeF_4 was taken in solution (in minimum amount of water) in a beaker and 25.2 c.c. of NaOH (0.1169 *N*) was added to it dropwise with constant stirring so that the molar ratio of K_2BeF_4 : NaOH was 1:1. Gelatinous precipitate (A) was found to appear almost from the beginning of the addition of caustic soda. Paper pulp was added to the solution and it was filtered carefully by suction through a rapid filtration quantitative filter paper (containing paper pulp) placed on a No. 3 sintered glass funnel. The filter paper was not washed to avoid the possibility of hydrolysis of the product (if any) in the precipitate. The filter paper was pressed with the head of a glass rod and was then ignited and fused with Na_2CO_3. The melt was taken in solution by hot water and the beryllium oxide (B) was freed of all soluble salts by leaching with hot water and then estimated. The amount of Be (13.07 mg.) calculated from (B) was found to weigh almost half of the total beryllium in the K_2BeF_4 taken. The filtrate after separation of (B) was found to contain almost no fluorine by PbClF method. The filtrate (C), obtained after separation of (A), was evaporated to dryness in a platinum basin and then fused with Na_2CO_3 (D). The BeO from (D) was estimated and the amount of Be (12.31 mg.), calculated from this, was also found to weigh almost half of the total amount of beryllium in the K_2BeF_4 taken. From the filtrate of this carbonate fusion (D), fluorine was estimated by PbClF method and found to be 209.9 mg. Thus, almost all of the fluorine of the K_2BeF_4 taken was in the filtrate (C) and the ratio of Be and fluorine in (C) was found to be 1 : 8. The total amounts of Be (25.38 mg.) and F (209.9 mg.), which were found out in the above experiments, were slightly less than the actual amounts of Be (26.5 mg.) and F (223.8 mg.) contained in the K_2BeF_4 taken. As the author's intention was to find out only the ratios of Be and F in the gelatinous precipitate (A) and in the filtrate (C), the beaker of precipitation, the sintered funnel and the Büchner flask were not washed because this was thought to be unnecessary. Thus, the low results obtained above can be accounted for. So, from this experiment it was found that when K_2BeF_4 and NaOH were mixed in equimolar amounts, half of the total K_2BeF_4 was decomposed with the precipitation of $Be(OH)_2$, leaving the other half unchanged, and no K_2BeF_3OH was formed in the process.

DISCUSSION

It is observed from the conductometric titration curves I and II that the inflection points correspond to the molar ratios of K_2BeF_4 : NaOH as 1 : 2, so that the reaction occurs according to the equation

$$K_2BeF_4 + 2\,NaOH = Be(OH)_2 + 2\,KF + 2\,NaF \qquad \ldots\ (1)$$

FIG. 1

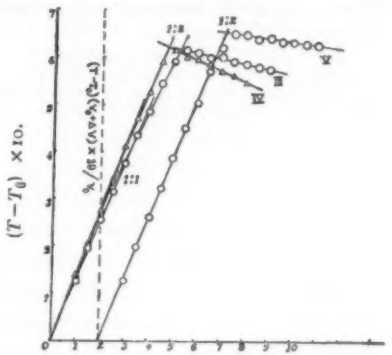


NaOH *soln. added in c c.*

Curve I : 100 c.c. of 0 001 *M*-K_2BeF_4 soln. + 0.1 *M*-NaOH soln.

II : 50 c.c. of 0 0404 *M*-K_2BeF_4 + 0.808*M*-NaOH soln.

FIG. 2



NaOH *soln. added in c.c.*

Curve III : 100 c.c of *M*/15-K_2BeF_4 soln. + 2.436 *M*-NaOH.

IV : 100 c.c. (approx) soln. containing 1.1023 g. of K_2BeF_4 + 2.9223*M*-NaOH.

V : 100 c c. of *M*/15-K_2BeF_4 soln. + 2.436 *M*-NaOH (plotted after vol. correction).

In the thermometric titration curves III and IV two breaks are found to appear. The first and second breaks correspond respectively to the molar ratios of K_2BeF_4 : NaOH = 1 : 1 and 1 : 2. The first break was explained by Mitra (*loc. cit.*) as due to the formation of K_2BeF_3OH. But it is noticed that when curve V is drawn with the same data of curve III after making volume correction according to Chatterjee (*loc.cit.*), the break at 1:1 disappears. It can be pointed out in this connection that the data represented by Mitra (*loc.cit.*) are not in agreement with those of the present author and are not understandable as can be seen by comparing with the present one. It will be observed in curve V that the inflection point occurs at molar ratio of K_2BeF_4 : NaOH = 1 : 2 and then temperature gradually falls probably due to the formation of beryllate ion by the gradual dissolution of $Be(OH)_2$ in excess of alkali ; the reaction occurring probably is an endothermic one.

Again, by the addition of one mole of NaOH to one mole of K_2BeF_4 and analysing the products (*vide supra*), it was found out that $Be(OH)_2$ was precipitated by decomposition of K_2BeF_4 according to equation (1) and no K_2BeF_3OH was formed in the process.

So, from the above evidence it has been definitely shown that the primary reaction between caustic soda and fluoberyllate ion occurs according to equation (1) and the secondary reaction, *i.e.* the dissolution of $Be(OH)_2$ in excess of alkali, occurs subsequently, forming beryllate ion no indication of the formation of $[BeF_3OH]''$ ion has been found.

The author's best thanks are due to Prof. P. B. Sarkar, Dr.es.Sc., F.N.I., Head of the Department of Pure Chemistry and the Ghosh Professor of Chemistry, for his encouragement and suggestions in the work. He is also indebted to Sri N. N. Ghosh of Pure Chemistry Department for his suggestions.

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Received December 9, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 6, 1956]

SEARCH FOR NEW INSECTICIDES. PART XI. SYNTHESIS OF SUBSTITUTED ωω-DICHLOROACETOPHENONES

By A. B. Sen and A. K. Sen Gupta

Several alkyl- and halogen-substituted phenolic esters of dichloroacetic acid and the corresponding *o*-hydroxy-ωω-dichloroacetophenones have been prepared with a view to studying their insecticidal activity.

It has been observed by Tiwari and Tripathi (this *Journal*, 1956, **33**, 214) that phenolic esters of chloroacetic acid as well as the *o*-hydroxy-ω-chloroacetophenones derived from them are very active against house fly. Dormal, Delvaux and Dills (*J. Econ. Entomol.*, 1950, **43**, 915) have found that chlorination of phenols increases their insecticidal efficiency. We have therefore prepared a number of phenolic esters of dichloroacetic acid and *o*-hydroxy-ωω-dichloroacetophenones by the Fries migration of these esters. The ketonic and the ester groupings present in these compounds being lipophilic and the hydroxy grouping, hydrophilic in nature, the esters and the phenolic ketones are expected to possess insecticidal activity (Lauger *et al.*, *Helv. Chim. Acta*, 1944, **27**, 918).

The phenolic esters of dichloroacetic acid were prepared in the usual way by refluxing the appropriate phenols and dichloroacetyl chloride in benzene in presence of dry magnesium (Spasov, *Ann. Univ. Sofia*, II, Faculte phys-maths., 1938-39, **2**, 35, 289). The phenolic ketones were obtained by the Fries rearrangement of the above esters in the absence of a solvent, using 1.2 to 1.5 moles of anhydrous aluminium chloride. These ketones were characterised through their 2 : 4-dinitrophenylhydrazones.

The insecticidal activity of sixteen of these esters and hydroxyketones has been determined exclusively against laboratory-bred flies (*M. domestica*) using the topical method of application by a micrometer syringe. Some of these compounds show appreciable insecticidal activity, though inferior to the standard insecticides like D D T, when tested under identical conditions.

Experimental

Phenolic Esters of Dichloroacetic Acid.—To the appropriate phenol (0.1 *M*) in 20-25 c.c. of anhydrous benzene clean and dry magnesium ribbon in the form of a spiral was added. Dichloroacetyl chloride (0.1 *M*) was then added dropwise and the mixture was refluxed on the water-bath until HCl had ceased to evolve. The completion of the reaction took nearly 10 to 12 hours. After cooling, water was added and the benzene layer separated. It was then washed with 1% NaOH solution and finally with water. The benzene extract was dried over anhydrous calcium chloride and the benzene removed by distillation. The residual oil was distilled under reduced pressure. The esters, thus obtained, are summarised in Table I.

TABLE I

	Substituted phenyl dichloroacetates.	B. P.	Yield.	Formula.	%Carbon. Found.	%Carbon. Calc.	%Hydrogen. Found.	%Hydrogen. Calc.
1.	*o*-Chloro-	129°/1 mm.	75 %	$C_8H_5O_2Cl_3$	40.01	40.08	2.01	2.08
2.	2:4-Dichloro-	125°/2	86	$C_8H_4O_2Cl_4$	34.80	35.04	1.08	1.41
3.	2-Chloro 3-*tert.*-butyl-	173°/4	71	$C_{12}H_{13}O_2Cl_3$	47.89	48.73	3.96	4.93
4.	3:5-Dimethyl-	120°/4	76	$C_{10}H_{10}O_2Cl_2$	50.98	51.50	3.96	4.33
5.	3-Ethyl-	126°/2	81	$C_{10}H_{10}O_2Cl_2$	50.76	51.50	3.87	4.33
6.	2-*tert.*-Butyl-5-methyl-	145°/3	66	$C_{13}H_{16}O_2Cl_2$	55.77	56.70	5.08	5.81
7.	4-*tert.*-Butyl-	130°/8	76	$C_{12}H_{14}O_2Cl_2$	54.96	55.17	5.04	5.36
8.	4-*tert.*-Amyl-	140°/2	73	$C_{13}H_{16}O_2Cl_2$	55.56	56.70	5.17	5.81
9.	4-*sec.*-Amyl-	135°/4	74	$C_{12}H_{16}O_2Cl_2$	56.08	56.70	5.75	5.81
10	3-Methoxy-	139°/3	76	$C_9H_8O_3Cl_2$	40.96	41.70	2.98	3.40

Fries Rearrangement of the Esters.—The appropriate ester (1.0 *M*) was taken in a 500 c.c. round-bottomed flask, fitted with a reflux condenser and a calcium chloride guard tube. Finely powdered $AlCl_3$ (anhyd, 1.2 *M*) was added to it and the mixture was heated in an oil-bath at 120° for ½ hour. On decomposing the resultant puffy mass with ice and dilute HCl, an oil separated out (solids in the case of two esters which were filtered and recrystallised from hot alcohol). It was taken up in ether, washed successively with water, 1% sodium carbonate solution and finally with water. The ethereal layer was dried over anhydrous sodium sulphate and the ether removed by distillation. The residual oil was distilled under reduced pressure. The hydroxyketones obtained conformed to Pyman's test (*J. Chem. Soc.*, 1930, 280).

These ketones obtained were all converted into 2:4-dinitrophenylhydrazones, which were recrystallised from hot glacial acetic acid. The b.p., m.p., yield and percentage of nitrogen of the compounds so obtained are recorded in Table II,

TABLE II

	Substituted *o*-hydroxyl-dichloroacetophenones.	B. P.	Yield.	2:4-Dinitrophenylhydrazones. M. P.	Formula.	% Nitrogen. Found.	% Nitrogen. Calc.
1.	3-Chloro-	173°/8 mm.	76%	160°	$C_{14}H_9N_4O_5Cl_3$	10.33	10.96
2.	3:5-Dichloro-	(m.p.) 90°	50	149°	$C_{14}H_8N_4O_5Cl_4$	11.97	12.44
3.	3-Chloro-5-*tert.*-butyl-	175°/20	79	130°	$C_{18}H_{17}N_4O_5Cl_2$	11.15	11.77
4.	4:6-Dimethyl-	150°/4	58	145°	$C_{16}H_{14}N_4O_5Cl_2$	12.87	13.55
5.	5-Ethyl-	110°/8	53	230°	$C_{16}H_{14}N_4O_5Cl_2$	12.84	13.55
6.	3-*tert.*-Butyl-6-methyl-	88°/6	60	145°	$C_{19}H_{20}N_4O_5Cl_2$	11.94	12.30
7.	5-*tert.*-Butyl-	120°/10	86	150°	$C_{18}H_{17}N_4O_5Cl_2$	11.84	12.73
8.	5-*tert.*-Amyl-	122°/2	54	140°	$C_{19}H_{20}N_4O_5Cl_2$	11.96	12.31
9.	5-*sec.*-Amyl-	125°/10	43	145°	$C_{19}H_{20}N_4O_5Cl_2$	11.97	12 31
10.	4-Methoxy-	(m.p.) 84°	42	201°	$C_{15}H_{12}N_4O_5Cl_2$	12.98	13.49

Bioassay of the Insecticidal Action.—Compounds recorded in Table III were tested for contact insecticidal activity against laboratory-bred house flies (*M. domestica*) in the following way :

A solution of the compound (10%) was made in acetone and applied topically to house flies (4-6 days old) with a microsyringe. A volume of 0.001 c.c. was applied to each fly on its back. After treatment the flies were transferred to a wire-mesh cage and held for observation. The rate of mortality was estimated according to Abbot's formula. Details of the experiments are shown in Table III.

TABLE III

No. of flies taken = 25. Dose per individual = 0.001 ml.

	Mortality after 24 hrs.	Corrected percentage.		Moralify atter 24 hrs.	Cor:ected percentage
Phenyl dichloroacetates:			*o*-Hydroxy-ω-dichloroacetophenones.		
2-Chloro-	12	46	3-Chloro-	10	37
2:4-Dichloro-	10	37	3-Chloro-5-*tert.*-butyl-	13	52
2-Chloro-4-*tert.*-butyl-	5	24	4:6-Dimethyl-	17	56
3:5-Dimethyl-	4	...	5-Ethyl-	18	70
3-Ethyl-	5	24	3-*tert.*-Butyl-6-methyl-	13	50
5-Methyl-3-*tert.*-butyl-	8	22	5-*tert.*- Amyl-	10	37
4-*tert.*-Butyl-	13	50	5-*tert.*-Butyl-	6	20
4-*tert.*-Amyl-	11	42	5-*sec.*-Amyl-	10	37
			D D T	25	100

The authors wish to thank the Director, Central Laboratories for Scientific and Industrial Research, Hyderabad for kindly permitting the bioassay of these insecticides done in his laboratory and Dr. M. B. Naidu of the above laboratory for carrying out the bioassay.

CHEMICAL LABORATORIES,
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LUCKNOW.

Received May 5, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 6, 1956]

INTERACTION OF AROMATIC HYDROXYKETONES AND THEIR DERIVATIVES WITH THIONYL CHLORIDE IN PRESENCE OF FINELY DIVIDED COPPER. PREPARATION OF 3:3'-DIPROPIONYL-4 :6-4':6'-TETRAHYDROXYDIPHENYL THIOETHER AND ITS DERIVATIVES FROM RESPROPIOPHENONE *

By V. J. Dalvi and G. V. Jadhav

Preparation of 3 :3'-dipropionyl-4 :6-4' :6'-tetrahydroxydiphenyl thioether and of diacetoxy dimethoxy, tetra-acetoxy and tetramethoxy derivatives of the thioether are described. Nitration, bromination as well as 2 :4-dinitrophenylhydrazone of the tetrahydroxy thioether are described.

The present work is the continuation of the work of Jadhav and Merchant (this *Journal*, 1951, **28**, 265). The reaction was carried out in presence of dry chloroform at room temperature, when the thioether was obtained. Its constitution was arrived at by the action of nitric acid below 5° on it, when 5-nitrorespropiophenone was obtained which showed that the two nuclei were linked through sulphur atom in the position *para* to -OH group and *meta* to -COEt group.

Bromination of the thioether in acetic acid medium furnished a dibromo derivative which on nitration in acetic acid medium afforded 3-bromo-5-nitrorespropiophenone. With excess of liquid bromine, the thioether afforded 2:4:6-tribromoresorcinol, which showed that liquid bromine broke the sulphur linking, oxidised the ketonic group to carboxyl group which ultimately lost carbon dioxide ; the resulting resorcinol was brominated.

Diacetoxy, tetra-acetoxy, dimethoxy and tetramethoxy derivatives as well as 2:4-dinitrophenylhydrazone of the thioether were prepared.

The mechanism of the reaction can be explained after Hirwe, Jadhav and Chakradeo (*J. Amer. Chem. Soc.*, 1935, **57**, 101), as the same thioether is also formed by the interaction of sulphur monochloride or sulphur dichloride and the ketone.

Experimental

3:3'-Dipropionyl-4 :6-4':6'-tetrahydroxydiphenyl Thioether (I).—Respropiophenone (12 g.) was suspended in dry chloroform (80 c.c.) and thionyl chloride (12 c.c.) was added to it, followed by gradual addition of finely divided copper (8 g., 1 hour) and left overnight at room temperature. The solution was filtered and the residue was repeatedly washed with dry chloroform. Brownish red paste, left over after removal of the chloroform at room temperature, was boiled with water for 1 hour. The dark red semi-solid obtained was first crystallised from acetic acid and then from benzene in pinkish white needles, m.p. 161-62°, yield 4 g. (Found : C, 59.5 ; H, 5.25 ; S, 8.7. $C_{18}H_{18}O_6S$ requires C, 59.7 ; H. 4 97; S, 8.8 per cent).

* This communication is to be treated as Part VI of this series.

It developed a red coloration with alcoholic ferric chloride solution and it dissolved in dilute NaOH solution with a yellow colour. It is easily soluble in acetone, moderately so in benzene, chloroform and acetic acid, and very sparingly in petroleum ether.

The same thioether was obtained by the interaction of the ketone (3 g.) and sulphur monochloride (1 c.c.) or sulphur dichloride (1.5 c.c.) in presence of dry ether (40 c.c.), the addition being done below 5° and allowing the reaction to proceed for 1 hour at room temperature, the yield being 0.3 g. and 0.7 g. respectively.

3 : 3′-*Dipropionyl*-4 : 4′-*dihydroxy*-6 : 6′-*diacetoxydiphenyl thiother* separated out when pyridine (1 c.c.) was added to the hot solution of the thioether (I, 1 g.) in acetic anhydride (10 c.c.). It crystallised in colorless needles from acetic acid, m.p. 216-17°. (Found : S, 7.1. $C_{22}H_{22}O_8S$ requires S, 7.2 per cent).

It gave a bottle-green coloration with alcoholic ferric chloride solution and dissolved in dilute alkali with a yellow colour.

If the above reaction mixture was heated on a boiling water-bath, instead of allowing it to cool, for 1 hour and then poured into dilute HCl and ice mixture, 3 : 3′-*dipropionyl*-4 : 6-4′ : 6′-*tetra-acetoxydiphenyl thioether* was obtained, crystallising from rectified spirit in colorless needles, m.p. 125-26°. (Found : S, 5.9. $C_{26}H_{26}O_{10}S$ requires S, 6.04 per cent).

It was insoluble in alkali and developed no coloration with alcoholic ferric chloride solution.

3 : 3′-*Dipropionyl*-4 : 4′-*dihydroxy*-6 : 6′ *dimethoxydiphenyl thioether* (II) was prepared by methylating (I) with dimethyl sulphate (1 : 1) in presence of alkali at 100°. It crystallised from acetic acid in pale yellow plates, m.p. 202 203°. (Found : S, 8.5. $C_{20}H_{22}O_6S$ requires S, 8.2 per cent).

It developed a bottle-green coloration with alcoholic ferric chloride and dissolved in dilute alkali with a yellow colour.

Methylation with excess of dimethyl sulphate under similar conditions afforded 3 : 3′-*dipropionyl*-4 : 6-4′ : 6′-*tetramethoxydiphenyl thioether*. It crystallised from alcohol in colorless needles, m.p. 197-98°. (Found : S, 7.5. $C_{22}H_{26}O_6S$ requires S, 7.6 per cent).

The thioether (II) was also obtained by the interaction of thionyl chloride (3 c.c.) and copper powder (2 g.) and 2-hydroxy-4-methoxypropiophenone (3.6 g.) at room temperature (yield 1.5 g.) and also by the action of sulphur monochloride (1 c.c.) or sulphur dichloride (1.5 c.c.) in presence of dry ether (50 c.c.) on 2-hydroxy-4-methoxypropiophenone with 0.5 g. and 1 g. yield respectively; in all cases the reaction was allowed to proceed overnight at room temperature.

2 : 4-*Dinitrophenylhydrazone* of (I) crystallised from acetic acid in dark red shining plates, m.p. 270° (decomp.). (Found : N, 15.6. $C_{30}H_{26}O_{12}N_8S$ requires N, 15.5 per cent).

2 : 4-*Dihydroxy*-5-*nitropropiophenone*.—The thioether (I, 1 g.) was gradually added to nitric acid (*d* 1.4, 10 c.c.) at about 5° and the reaction was allowed to proceed at that temperature for about 2 hours. The solid, obtained on diluting the reaction mixture with ice, crystallised from dilute alcohol in white needles, m.p. 131°. No depression in melting point was observed when mixed with an authentic specimen.

3 : 3′-*Dipropionyl*-4 : 6 : 4′ : 6′-*tetrahydroxy*-5 : 5′-*dibromodiphenyl Thioether* (III).—To the hot solution of the thioether (I, 3.5 g.) in acetic acid (25 c.c.) bromine solution in acetic acid (3 c.c., 10% w/v) was added. On cooling, the bromo derivative separated which crystallised from acetic acid in colorless needles, m.p. 212-13°, yield 2.5 g. (Found : Br, 30.7. $C_{18}H_{16}O_6Br_2S$ requires Br, 30.8 per cent).

3-*Bromo*-5-*nitrorespropiophenone*.—The thioether (III, 0.5 g.) was mixed with nitric acid (*d* 1.4, 2.5 c.c.) at about 5°. It was then heated for about 2 hours on a boiling water-bath and then diluted. The solid obtained was crystallised from acetic acid in colorless needles, m.p. 230-31°. (Found : Br, 27.5. $C_9H_8O_5NBr$ requires Br, 27.6 per cent).

Bromination of 5-nitrorespropiophenone (1 g.) in acetic acid with 8 c.c. of 10% bromine solution furnished the same product.

2 : 4 : 6-*Tribromoresorcinol*.—The thioether (I, 1 g.) was added to liquid bromine (5 c.c.) when it went into solution. Excess of bromine was removed next day and the solid obtained was washed with sodium bisulphite and crystallised from hot water, m.p. 111-12°. Mixed melting point with an authentic specimen, prepared according to Benedikt (*Monatsh.*, 1883, **4**, 227) showed no lowering.

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Received July 25, 1955.

[Jour. Indian Chem. Soc., Vol. 33, No. 6, 1956]

DISCONTINUITIES IN THE ADSORPTION OF POLYBASIC ACIDS FROM AQUEOUS SOLUTIONS ON ALUMINA GEL

By K. D. Jain and M. K. Jain

Further studies of the adsorption of polybasic acids (oxalic, succinic, tartaric, citric) by alumina gel under simular conditions show that the adsorption of monobasic acids on alumina gel is continuous, while that of polybasic acids is discontinuous and irregular, exhibiting maximum and minimum points at different equilibrium concentrations.

Dewey (*J. Phys. Chem.*, 1932, **36**, 3187) studied the adsorption of oxalic and acetic acids on alumina gel and found no compound formation in either case, and observed that oxalic acid was adsorbed very strongly at low concentrations. The adsorption isotherms drawn by him are continuous, provided that a considerable number of points are left without joining, otherwise it is quite irregular. Sen (*ibid.*, 1927, **31**, 680) found freshly precipitated aluminium hydroxide to develop a very high adsorptive power for acids.

Experimental

Preparation and Activation of Alumina Gel.—Aluminium hydroxide was obtained as a flocculent gelatinous precipitate by slow addition of ammonium hydroxide under vigorous stirring to a solution of aluminium sulphate at 24°. Yoe (*J. Amer. Chem. Soc.*, 1924, **46**, 2390) found that a higher temperature of precipitation was detrimental to the adsorptive power of the gel. This was washed free of all impurities. The process of filtration and purification appeared difficult and took about 25 days. It has now been obtained in a hard, glass-like form by slow-drying in an air-oven at 60-70°. As regards the suitable temperature of roasting, there is, however, no unanimity. Perry (*J. Phys. Chem.*, 1925, **29**, 1462) used a temperature of 200°; Munro and Johnson (*Ind. Eng. Chem.*, 1925, **17**, 88) activated alumina gel at 400°; Wood *et al.* (*ibid.*, 1926, **18**, 169) activated it at 1000°, and Dunstan and others (*J. Soc. Chem. Ind.*, 1924, **43**, 179T) recommended 600°-700° for bauxite. We activated alumina gel at 280°-290° according to Chowdhury and Bagchi (this *Journal*, 1928, **5**, 111) for about 4 hours. The water content of the gel on ignition was found to be 14.32%.

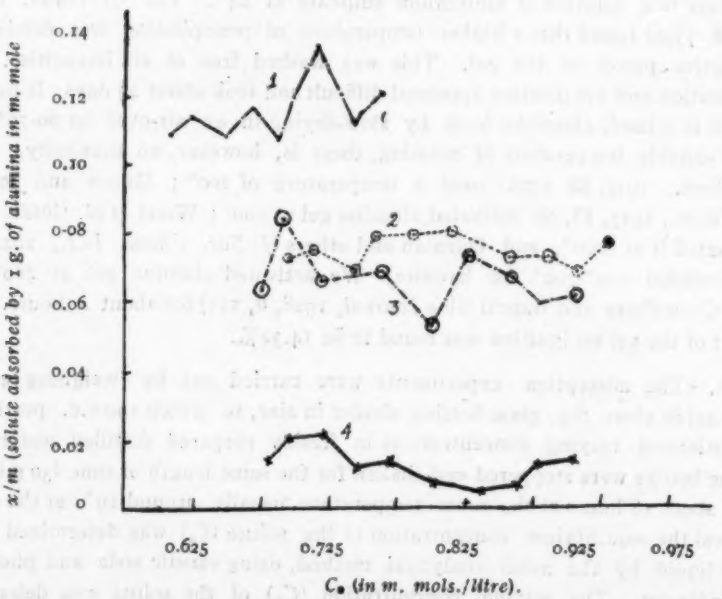
Analysis.—The adsorption experiments were carried out by weighing exactly 0.5 g. of the gel in clear, dry, glass bottles, similar in size, to which 100 c.c. portions of the acid solutions of varying concentrations in freshly prepared distilled water were pipetted. The bottles were stoppered and shaken for the same length of time (30 minutes) and kept for about 18 hours at the room temperature usually around 19°, at the end of which interval the equilibrium concentration of the solute (C_e) was determined in the supernatant liquid by the usual analytical method, using caustic soda and phenolphthalein as indicator. The original concentration (C_o) of the solute was determined under the same conditions from the blank experiment (without gel). The amount of

adsorption (x) was determined by difference (C_0-C_e) for 100 c.c. of the aqueous solutions ; x/m, the amount of adsorption per g. of alumina gel, was then calculated. Equilibrium concentration was calculated in millimoles per litre. The experiments were repeated with every care. The points in many cases were taken very close together and the estimation of the acids at these points was followed by a special method (Kolthoff and Furman, "Potentiometric Titrations", 1926, p. 148) as described below.

At the end of the burette a jet of fine bore was attached by a small piece of rubber tubing to reduce the volume of one drop. The volume of one drop was found out by counting the number of droplets in a certain known volume of liquid (water). The average of a number of experiments was taken, and the volume of one drop was found to be 0.025 c.c., *i.e.*, 4 drops were equal to 0.1 c. c.

In the previous work (this *Journal*, 1940, **17**, 685 ; 1941, **18**, 321, 585 ; 1953, **30**, 772) on adsorption of polybasic acids, bi-salts and hydroxybenzenes by activated sugar charcoal and silica gel, the adsorption was found to be highly influenced by the basicity of the acids. Results obtained by the present study confirm the previous observation (*loc. cit.*). It is found that the adsorption isotherm in the case of monobasic acids is invariably a straight line, while in the case of polybasic acids, zigzag curves (Fig. 1) are obtained which appear to be periodic. Dewey (*loc. cit.*) would have arrived at similar zigzag curves for oxalic acid on alumina gel if he had joined all the points.

FIG. 1



Curves 1-4 refer respectively to oxalic, citric, tartaric and succinic acid.

In each case the differences between the equilibrium molar concentrations at the maxima and minima points are multiple with few exceptions. This may be due to the fact that they might be displaced from their right places.

Electrometric study of the rate of adsorption of acids by sugar charcoal (*loc. cit.*) suggested the complexity occurring on the surface of the adsorbent. It is also found that the curves are not reproducible in detail, indicating the adsorbent surfaces of different activity. Further work is in progress to find out some explaination for these irregularities.

The authors are thankful to Principal Dr. R. N. Saksena and Prof. L. N. Gupta for providing facilities for the work.

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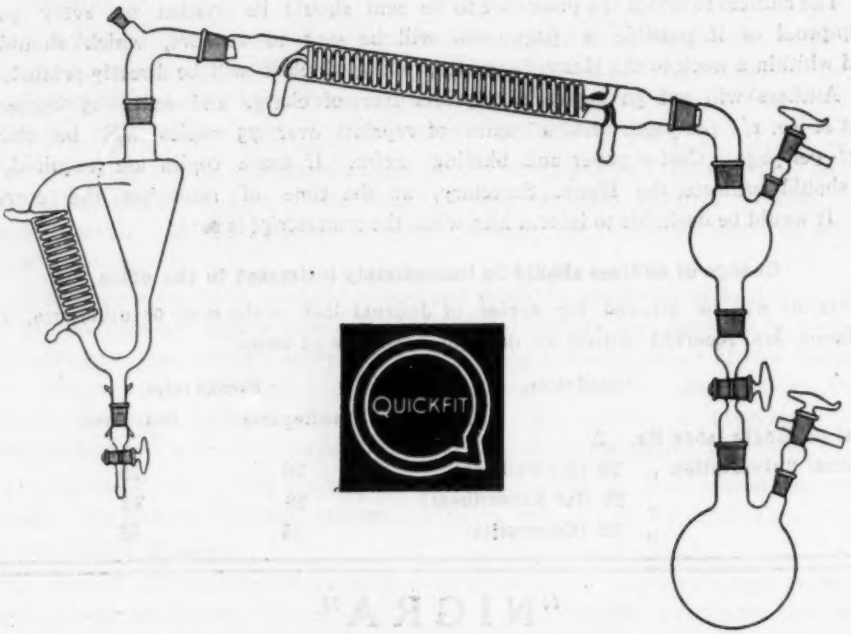

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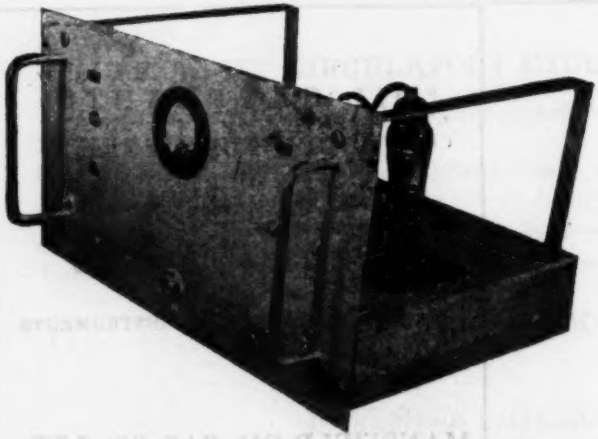

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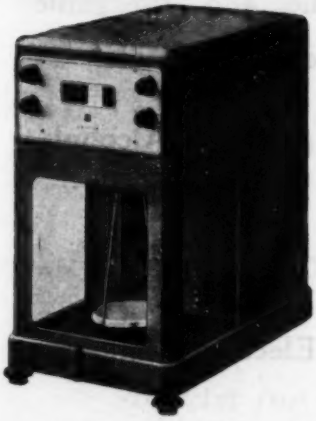

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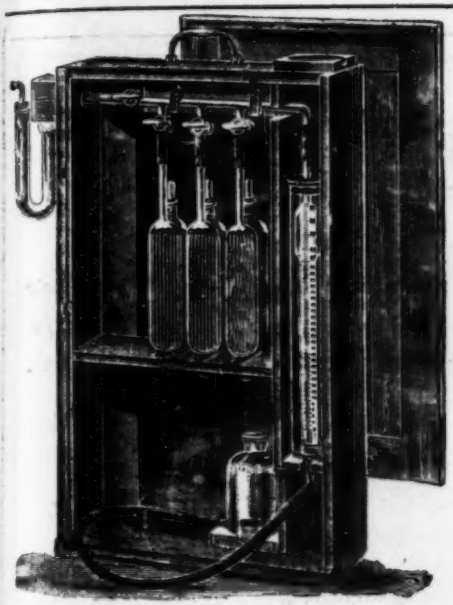

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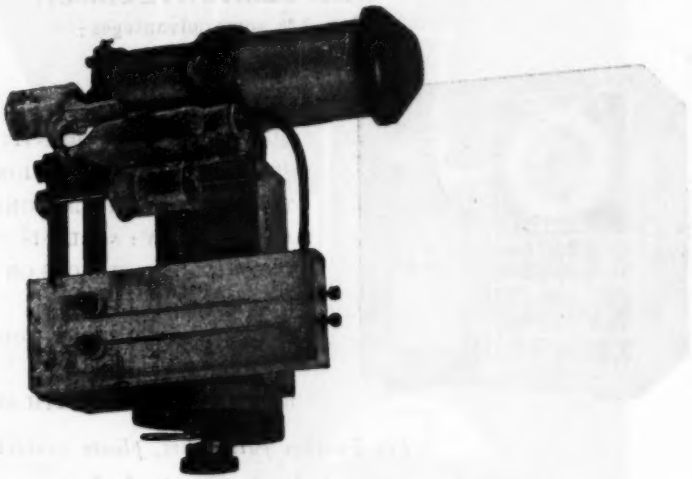

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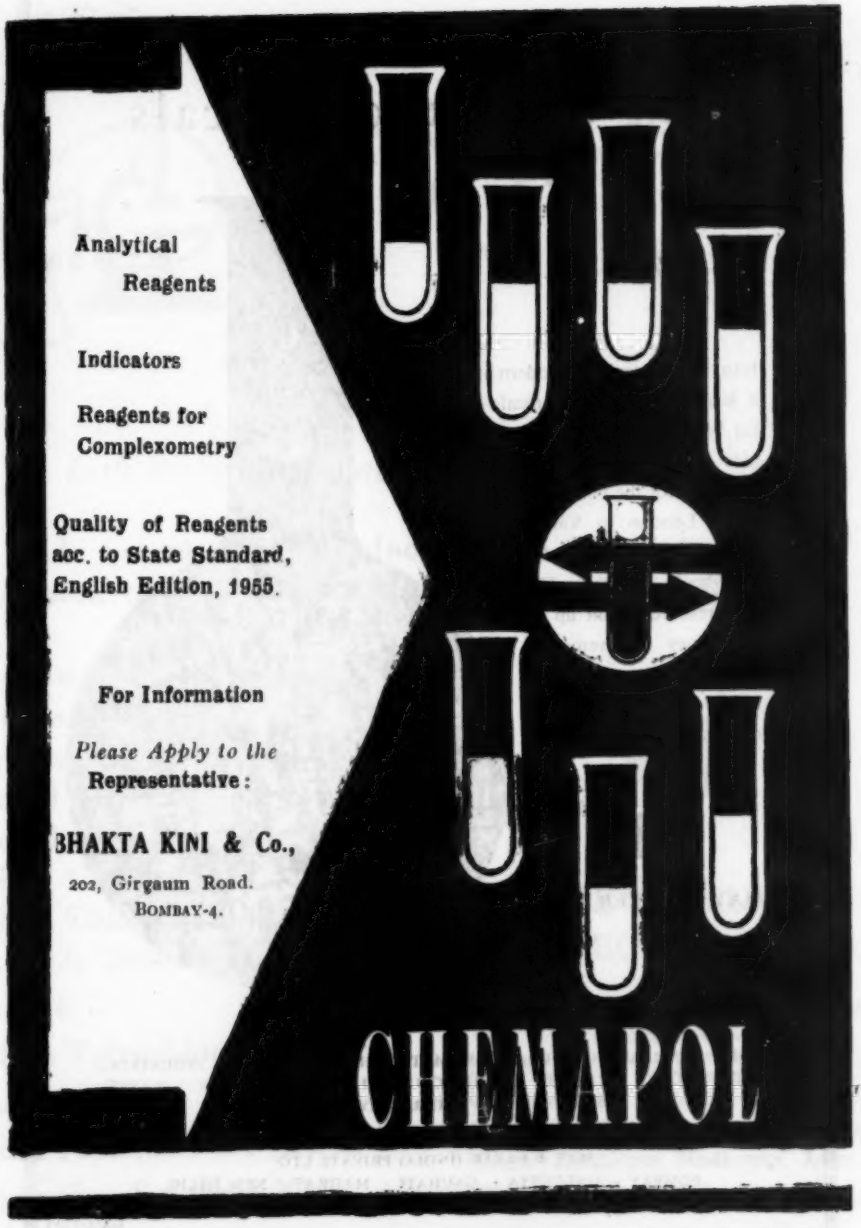

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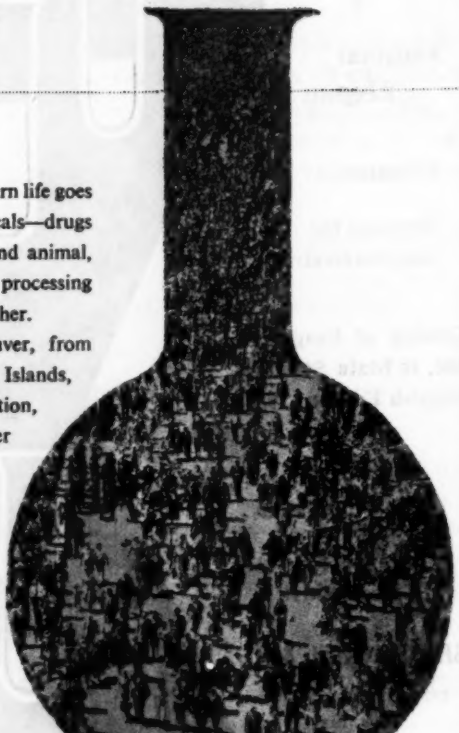

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